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HAND-BOOK

OF

CHEMISTRY.

BY

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VOL. II.

NON-METALLIC ELEMENTS.

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EXPLANATION OF THE SHORT TABLES WHICH OCCUR IN THIS AND THE SUBSEQUENT VOLUMES.

The table which gives the composition of nitric oxide (p. 377) may serve as an example:

	Calculation.		*d.*	*d.*	*d.*
a.	*b.*	*c.*	H. Davy.	Dalton.	Berzelius.
N	14	46·67	42·3	42	46·754
2O	16	53·33	57·7	58	53·246
NO^2	30	100·00	100·0	100	100·000

	f. Vol.	*g.* sp. gr.		*h.* Vol.	sp. gr.
Nitrogen gas	1	0·9706	=	$\frac{1}{2}$	0·4853
Oxygen gas	1	1·1093	=	$\frac{1}{2}$	0·5546
Nitric oxide gas	2	2·0799	=	1	1·0399

a. The constituents of nitric oxide are nitrogen and oxygen; and they are most probably united in the proportion of 1 atom of nitrogen to 2 atoms of oxygen.

b. According to the most accurate experiments hitherto made on the proportions by weight in which nitrogen and oxygen combine with each other and with other bodies, the atomic weight of nitrogen is estimated at 14, that of oxygen being assumed = 8, and that of hydrogen = 1. Moreover, since the atomic weight of a compound is found by adding together the atomic weights of its element, the atomic weight of nitric oxide must be $14 + 2 . 8 = 30$.

c. If 30 parts of nitric oxide contain 14 nitrogen and 16 oxygen, it follows that 100 nitric oxide will contain 46·67 nitrogen and 53·33 oxygen.

d, d, d. The analyses of different chemists here given, calculated to 100 parts, serve, on the one hand, to establish the correctness of the calculation *c*, made upon a particular stoïchiometrical hypothesis, and, on the other hand, are themselves confirmed by that calculation: viewed in this light, the analysis of Berzelius appears to be more correct than that of Davy or Dalton.

e. Gaseous bodies likewise exhibit great simplicity and regularity, when their composition is estimated by volume. (I. 64—67.)

f. In the case under consideration, 1 volume of nitrogen gas combines with exactly 1 volume of oxygen gas to form 2 volumes of nitric oxide gas, without condensation.

g. Hence, if the specific gravities of oxygen and nitrogen gases are known, that of nitric oxide gas may be calculated from them. And since it is known that if a given volume of atmospheric air weighs 1·0000 grain, an equal volume of oxygen gas will weigh 1·1093 gr., and an equal volume of nitrogen gas 0·9706 gr., and that 2 vol. nitrogen gas and 1 vol. oxygen gas form 2 vol. nitric oxide gas—it follows that 2 volumes of nitric oxide gas must weigh as much as 1 vol. nitrogen gas and 1 vol. oxygen gas together, viz., $0·9706 + 1·1093 = 2·0799$.

h. Lastly, since, according to the preceding, 1 volume of nitric oxide gas contains ½ vol. nitrogen + ½ vol. oxygen, it follows that by adding half the specific gravity of nitrogen gas to half the specific gravity of oxygen gas, we shall obtain the specific gravity of nitric oxide gas; $\frac{0.9706}{2} + \frac{1.1093}{2} = 1.0399$.

Chemical Formulæ.—The composition of bodies is explained sometimes by schemes, sometimes by formulæ. The former explain themselves. To facilitate the understanding of the latter—for which purpose, when they are rather long, mere inspection is not sufficient—the following means may be used:

1. Convert the formula into a scheme, (*a*) by placing opposite to each other, in the most convenient manner possible, the substances contained in the first part of the formula, with their proper numbers of atoms, the combined substances being connected by dotted lines; and (*b*) denoting the newly formed compounds according to the second side of the formula, by full connecting lines.

As an example, take the conversion of chlorate of potash by oil of vitriol into bisulphate and perchlorate of potash and chloric oxide gas:

$$3(KO, ClO^5) + 4SO^3 = 2(KO, 2SO^3) + KO, ClO^7 + 2ClO^4.$$

a.				*b.*			
$2SO^3$	KO	OOOOOCl		$2SO^3$	KO	O	OOOOCl
$2SO^3$	KO	OOOOOCl		$2SO^3$	KO	O	OOOOCl
	KO	OOOOOCl			KO	O	OOOOCl

This method is the most circumstantial, but at the same time the clearest.

2. *a.* Add together the several constituents of each half of the formula, and see whether the two sums are equal:

		K	O	Cl	S
First half:	$3(KO, ClO^5)$	3	18	3	
	$4SO^3$		12		4
		3	30	3	4
Second half:	$2(KO, 2SO^3)$	2	14		4
	KO, ClO^7	1	8	1	
	$2ClO^4$		8	2	
		3	30	3	4

b. Or, add together the elements of the first half of the formula, and from the sum thus obtained, deduct the elements of the products of decomposition, one by one:

		K	O	Cl	S
$3(KO, ClO^5) + 4SO^3$	=	3	30	3	4
$-2(KO, 2SO^3)$		2	14		4
	=	1	16	3	
$-KO, ClO^7$		1	8	1	
$= 2ClO^4$			8	2	

PART II. (*continued.*)

SPECIAL CHEMISTRY,

OR

THEORY OF THE AFFINITY OF INDIVIDUAL SUBSTANCES.

SECTION II.

Chemistry of Ponderable Bodies.

The number of undecomposed ponderable substances at present known to exist is 61. These bodies may be divided into Metalloids or Non-metallic Elements, and Metals.

12 Non-metallic Elements: Oxygen, Fluorine, Chlorine, Bromine, Iodine, Selenium, Sulphur, Phosphorus, Boron, Carbon, Hydrogen, and Nitrogen.

49* Metals: Potassium, Sodium, Lithium, Barium, Strontium, Calcium, Magnesium, Lanthanum, Didymium, Cerium, Yttrium, Erbium, Terbium, Glucinum, Aluminum, Thorinum, Zirconium, Silicium, Titanium, Tantalium, Niobium, Pelopium, Tungsten, Molybdenum, Vanadium, Chromium, Uranium, Manganese, Arsenic, Antimony, Tellurium, Bismuth, Zinc, Cadmium, Tin, Lead, Iron, Cobalt, Nickel, Copper, Mercury, Silver, Gold, Platinum, Palladium, Rhodium, Iridium, Ruthenium, and Osmium.

No exact line of demarcation can be drawn between metals and metalloids; silicium is sometimes regarded as a non-metallic body; and iodine and bromine as metals.

The elementary bodies may be arranged in groups according to their physical and chemical relations; and these groups may be again arranged according to their more general resemblances. The following is an imperfect attempt of this kind. The only way of making a satisfactory arrangement would be to dispose the elements, not on a plane surface, but within an envelope of three dimensions.

```
  O                           N                        H
F Cl Br I                                          L  Na   K
  S Se Te                                         Mg Ca Sr Ba
    P  As Sb                              G Er Y Tr Ce  Di La
       C  B  Si                                 Zr Th Al
    Ti Ta Nb Pe W                             Sn Cd Zn
               Mo V Cr        U     Mn Co Ni Fe
                    Bi   Pb   Ag    Hg Cu
                 Os Ru   Ir   R     Pt Pd   Au
```

* Or perhaps 51,—the existence of two other metals, Norium and Ilmenium, having lately been shown to be probable. This would make the total number of elements 63, instead of 61. [W.]

Those substances which stand next to one another in the same row, resemble each other in certain respects. Oxygen, Hydrogen, and Nitrogen stand alone; there is no known element analogous to either of them. The groups of electro-negative elements are placed on the left; those of the electro-positive elements, on the right.

The above-named elements form with one another two classes of compounds—the *Organic* and the *Inorganic*. All the elements are capable of entering into inorganic combinations; but only a few of them—more especially Carbon, Hydrogen, Oxygen, and Nitrogen,—likewise form organic compounds. Moreover, inorganic compounds are produced in the so-called inanimate world, and may be formed artificially from inorganic materials. Organic compounds, on the contrary, originate almost exclusively in plants and animals. Art may indeed convert one organic compound into another, but it is only in a very few cases that such compounds can be formed artificially from inorganic materials.

Common salt, nitre, glass, brass, &c. are inorganic; sugar, alcohols, fats, resins, glue, &c. are organic compounds. A more exact discrimination of the two classes will be given in the Introduction to Organic Chemistry.

FIRST DIVISION.

Chemistry of Inorganic Compounds,

OR

INORGANIC CHEMISTRY.

Inorganic Compounds are:

I. *Compounds of the First Order,*

i.e. compounds of two simple substances: and these may be arranged—

(1.) According to the relative numbers of their atoms.

A. One atom of the one substance combines with one atom of the other, *e.g.* HO, CO, HCl, KO, NaS, &c.

B. 1 At. with 2 At. *e.g.* HO^2, CO^2, SO^2, PbO^2, KS^2.

C. 1 At. with 3 At. *e.g.* BO^3, PO^3, SO^3, CrO^3, PCl^3, NH^3, $SbCl^3$.

D. 1 At. with 4 At. *e.g.* NO^4, ClO^4, NH^4, OsO^4.

E. 1 At. with 5 At. *e.g.* PO^5, ClO^5, SbO^5, PCl^5, $SbCl^5$.

F. 1 At. with 7 At. *e.g.* IO^7, ClO^7.

G. 2 At. with 3 At. *e.g.* Fe^2O^3, Cr^2O^3.

H. 2 At. with 5 At. *e.g.* S^2O^5.

I. 2 At. with 7 At. *e.g.* Mn^2O^7.

K. 3 At. with 4 At. *e.g.* Fe^3O^4, Mn^3O^4, Pb^3O^4.

L. 3 At. with 5 At. *e.g.* S^3O^5.

A few more complicated relations are likewise met with, *e.g.* Fe^7S^8, Fe^8O^9. It is a question, however, whether every inorganic compound

which contains more than one atom of each of its elements ought not to be regarded as a compound of the second order. Thus, S^2O^6 may be expressed by $SO^2 + SO^3$; S^3O^5, by $2SO + SO^3$, &c., &c. In the case of Mn^2O^7, such an alteration of the formula cannot however be admitted, so long as no higher degree of oxidation of manganese is known to exist.

(2.) According to the electro-negative element.

Compounds of Oxygen, — (*a*), with Metalloids, *e.g.* $HO, HO^2, CO, CO^2, PO^3, PO^5, SO^2$, &c.

(*b*) With Metals, *e.g.* $KO, KO^3, TiO^2, Cr^2O^3, CrO^3, AsO^3, AsO^5, PbO$.

Compounds of Fluorine: *Fluorides.*—(*a.*) With Metalloids, *e.g.* HF, BF^3.—(*b.*) With Metals, *e.g.* CaF, SiF^2.

Compounds of Chlorine: *Chlorides.*—(*a.*) With Metalloids, *e.g.* HCl, PCl^3, PCl^5, S^2Cl.—(*b.*) With Metals, *e.g.* $NaCl, Fe^2Cl^3, SnCl^2$.

The Compounds of Bromine and Iodine (*Bromides* and *Iodides*) correspond to those of Chlorine.

Compounds of Selenium; *Selenides* or *Seleniurets.*—(*a.*) With Metalloids, *e.g.* PSe, SSe.—(*b.*) With Metals, *e.g.* $KSe, PbSe$.

Compounds of Sulphur, *Sulphides* or *Sulphurets.*—(*a.*) With Metalloids, *e.g.* HS, HS^5, CS^2, PS. — (*b.*) With Metals, *e.g.* KS, FeS, AsS^3, AsS^5.

Compounds of Phosphorus and Carbon with Metals; *Phosphides* or *Phosphurets*, and *Carbides* or *Carburets.*

Compounds of Nitrogen, with Hydrogen, *e.g.* NH^3, and with Metals.

Compounds of a more electro-negative metal with a more electro-positive metal: simple alloys, *e.g. Arsenides, Tellurides, Antimonides*, &c.

(3.) According to the electro-positive element.

Compounds of Potassium, *e.g.* $KO, KO^3, KF, KCl, KBr, KI, KSe, KS$, $KS^2, KS^3, KS^4, KS^5, K^3P$. Similarly with the other metals.

Compounds of Hydrogen, *e.g.* $HO, HO^2, H^3P, HS, HS^5, HSe, HI$, $HBr, HCl, HF, H^3N, H^3As, HTe$. This group includes—amongst other compounds—all the inorganic Hydrogen-acids.

(4.) According to the physical and chemical relations of the compounds.

Difficult as it may appear to arrange all compounds of the first order in definite groups, according to this principle of classification, it is not the less obvious that the greater number of these compounds may, with more or less propriety, be divided into two classes, viz., those of *Inorganic Acids*, and *Inorganic Salifiable Bases.* The characters of these two classes are, in many of the compounds belonging to them, most decidedly marked; whereas, in many others they are so much modified as to throw considerable doubt on the exact chemical nature of the compounds to which they belong.

There appears also to be a gradual transition from the strongest acids through the weaker acids, and thence through the weaker bases to the strongest bases,—so that the idea of acid and base becomes merely relative. Alumina must be regarded as a base when in combination with sulphuric acid; but in combination with the much more strongly basic substance, potassa, it acts as a very weak acid. Compounds of this medium character, such as alumina, peroxide of tin, water, &c., are sometimes denominated *Amphoteric* compounds.

Inorganic Acids are more electro-negative than salifiable bases; and

when their compounds with these latter, or with water, are subjected to the action of the electric current, the acids—when not themselves decomposed—are evolved at the positive pole. They are mostly soluble in water—have a sour taste—many of them exert a corrosive action on organic substances—they redden the blue colour of litmus, and of various flowers, the violet for example,—exhibit great affinity towards salifiable bases, and neutralize them more or less. They are divided into *Oxygen-acids*, such as $CO^2, PO, PO^3, PO^5. SO, SO^2, SO^3, AsO^3, AsO^5$, &c.—and *Hydrogen-acids*, such as HF, HCl, HBr, &c. Since these more strongly marked acids all contain either oxygen or hydrogen, these two bodies may be regarded as the *Acidifying Principles;* the body combined with them is the *Radical of the Acid.*

Besides these, however, many compounds of Fluorine, Chlorine, Iodine, Selenium, and Sulphur with non-metallic elements, *e.g.* $BF^3, BCl^3, PCl^3, PCl^5, CS^2$, &c., and with the more electro-negative metals, *e.g.* $HgCl$, $PtCl^2, AsS^3, AsS^5$, &c., may be regarded as acids in the more extended sense.—although they are for the most part destitute of the above mentioned properties of acids, with the exception of their electro-negative character, and their power of combining with certain salifiable bases.

Inorganic Salifiable Bases are more electro-positive than acids; and, when their combinations with acids are subjected to the electric current, they are liberated at the negative pole. A few of them only are soluble in water; and in this case they are characterized by a taste different from that of acids, and by opposite actions on vegetable colours. They all exhibit affinity towards acids, and neutralize them more or less.

Almost all salifiable bases in the more restricted sense, are metallic oxides; in them the oxygen must be regarded as the *Basic Principle.* The same metal which, with a small quantity of oxygen, forms a base, *e.g.* MnO, may, when combined with a larger quantity of oxygen, produce an acid, *e.g.* MnO^3. In the base, the electro-positive nature of the metal exerts the greater power; in the acid, the electro-negative tendency of the oxygen has the advantage.

These basic metallic oxides may be divided into three classes.

Inorganic Alkalis. These oxides are soluble in water,—corrode animal substances,—have a soapy or urinous taste—change the colour of most blue or red flowers to green, the yellow colour of turmeric root to red,—and restore the blue colour of litmus which has been reddened by an acid. Of all bases they have the strongest affinity for acids, and neutralize them most completely. To this class belong KO, NaO, LO, BaO, SrO, CaO, and likewise ammonia, NH^3. Since, however, this last substance in its compounds is always associated with an atom of water, it may likewise be regarded as NH^4O. If ammonium, NH^4, be regarded as a compound metal, the oxide of ammonium, NH^4O, must also be looked upon as a metallic oxide.

Earths. These bodies are colourless, have a specific gravity below 4·000 or 5·000, are very difficultly fusible, not volatile, insoluble in water, tasteless, destitute of corrosive action, and have no effect on vegetable colours; they exhibit less affinity for acids than the alkalis do, and neutralize them less completely. To this class belong MgO, YO, GO, Al^2O^3, &c.

Salifiable Heavy Metallic Oxides. Many of these compounds are coloured, of a specific gravity higher than 5·000, easily fusible or volatile; some of them exhibit a certain degree of solubility in water, alkaline reaction, and metallic taste. Their affinity for acids is in some cases greater,

in others less, than that of the earths. This class includes: FeO, CuO, Hg^2O, HgO, Fe^2O^3, &c.

The alkalis, earths, and heavy metallic oxides exhibit many gradations one into the other, and no exact lines of demarcation can be drawn between them.

In this class also, as in that of acids, the compounds of fluorine, chlorine, bromine, iodine, selenium, sulphur, tellurium, arsenic, &c., with the more electro-positive metals, may be regarded as salifiable bases in the more extended sense.

II. *Compounds of the Second Order.*

1. Combinations of a Compound of the First Order with an Elementary Body.

To this division belong: CO, Cl,—SO^2, Cl,—S^2O^5, Cl,—CrO^2, Cl,—MoO^2, Cl, &c.

These compounds may be regarded in three different points of view: (1.) Phosgene, for example, CO, Cl, consists of carbonic oxide, CO, and chlorine; and, in fact, it is produced by bringing these two gases together under the influence of light.—(2.) Or it is a compound of carbonic acid, CO^2, with a bichloride of carbon, CCl^2, not yet isolated; according to this view, phosgene would be CO^2, CCl^2.—(3.) Or it is carbonic acid, CO^2, in which one atom of oxygen is replaced by an atom of chlorine,—therefore $COCl$.—According to the first and second of these views, phosgene is a compound of the second order; according to the third view, it is of the first order.—Similarly, SO^2, Cl may be represented as $2SO^3, SCl^3$, or as SO^2Cl;—also $S^2O^5, Cl=5SO^3, SCl^5=S^2O^5Cl$;—and $CrO^2, Cl=2CrO^3, CrCl^3=CrO^2Cl$, &c.

2. Combinations of one Compound of the First Order with another.

Simple Salts in the widest sense.

The electro-negative compound contained in these bodies may be regarded as the acid,—and the electro-positive compound as the base in the more extended sense.

A. *The two Compounds of the First Order contain a Common Element.*

(a) *Hydrates.* Compounds of water with oxygen acids, in which the water plays the part of a base: *e. g.* HO, SO^3,—and with salifiable bases, in relation to which it must be regarded as a weak acid: *e. g.* KO, HO. The combination generally takes place according to equal numbers of atoms. (Vid. *Hydrogen.*) These hydrates may be considered as belonging to the class of oxygen-salts.

(b) *Oxygen-salts.* Compounds of an oxygen-acid with a salifiable metallic oxide.—From the combination of alkalis with acids are derived the *Alkali-salts*, (*Alkali-oder Neutral-salze**); the earths in combination with acids yield the *Medium Salts* (*Mittel-salze*); and the heavy metallic oxides yield the *Heavy Metallic Salts*, or simply *Metallic Salts.*

The Oxygen-salts may be divided:

1. According to their Acid; into *Carbonates, Sulphates, Chlorates, Nitrates, Arseniates* &c.

* This term can scarcely be translated: we do not use the term *Neutral Salt* in the manner here indicated.

2. According to their Base; into salts of ***Ammonia, Potassa, Magnesia, Protoxide of Iron, Sesqui-oxide of Iron***, &c.

3. According to their taste and their action on vegetable colours. If they redden litmus and have a sour taste, they may be designated as *Acid Salts;* if they redden turmeric, and have an alkaline taste,—or at all events, if they contain a greater quantity of base than is necessary to neutralize the specific reaction of the acid,—they are called *Basic Salts;* and if they have neither an acid nor an alkaline reaction, the term *Neutral Salts* may be applied to them.

This mode of division, first introduced by Berthollet (*N. Gehl.* 3, 248), and still frequently employed, is of a very uncertain character. Insoluble salts generally appear neutral, merely in consequence of their insolubility, whatever may be the proportion of base and acid of which they are formed. Among the soluble salts, on the contrary, very few are perfectly neutral towards delicate reagents: thus, certain salts of the alkalis,—sulphate of lime, for example,—have a feeble alkaline reaction; and the salts of the earths and heavy metallic oxides,—if they only contain a sufficient quantity of acid to render them soluble in water, are for the most part slightly acid.

4. According to the number of atoms in which the acid and base are united: *Stoïchiometrical Classification.*

Either the acid and base are united in the normal proportion,—*Normal Salts**; or the salt contains an excess of acid,—*Acid Salts;* or an excess of base,—*Basic Salts.*

Normal Oxygen-salts. These salts generally contain one atom of base to one atom of acid; but there are certain acids which require more than one atom of base, and contain bases which require more than one atom of acid to form normal combinations. Hence acids and bases may be divided into the following groups.

Monobasic Oxygen-acids; e. g. $CO^2, SiO^2, TiO^2, SO^2, SO^3, ClO^5, NO^5$ Metaphosphoric acid$=a\,PO^5$. One atom of each of these acids takes up one atom of a mon-acid base.

Bibasic Oxygen-acids. The only acid possessing this property is the Pyrophosphoric, $b\,PO^5$. One atom of this acid combines with two atoms of a mon-acid base.

Tribasic Oxygen-acids. PO^3, ordinary Phosphoric acid$=c\,PO^5$, and AsO^5. One atom of each of these acids combines with one atom of a mon-acid base; and if this is not present, one or two atoms of water are taken up in place of one or two atoms of the deficient base.

$Al^2O^3, Cr^2O^3, Mn^2O^3$ and Fe^2O^3 seem likewise to belong to this group.

A great many of the organic acids are polybasic.

Metaphosphoric acid, pyrophosphoric acid, and ordinary phosphoric acid have all the same composition, viz. PO^5: they are isomeric (vid. Vol. I., p. 109). To distinguish between the formulæ of these acids, the letters *a, b, c,* are prefixed to them; *a,* the first letter of the alphabet, denotes that the acid is monobasic; *b,* the second, that it is bibasic; and *c,* the third, that it is tribasic.

Mon-acid Oxygen-bases. To this group belong all those which contain one atom of oxygen united to one or two atoms of metal: *e. g.* KO, MgO, Hg^2O, HgO. They form normal salts when they combine with

* Since normal salts often exhibit acid or alkaline reactions, and are, consequently, not neutral to the taste or to vegetable colours, I have, in order to avoid misconception, adopted the term *normal* instead of *neutral* for salts composed according to the regular preparation.

one atom of a monobasic acid; *e. g.* KO, CO^2,—NaO, SO^3,—Hg^2O, NO^5:—Of a bibasic acid, each atom requires two atoms of a mon-acid base; *e. g.* $2NaO, bPO^5$; and of a tribasic acid, each atom requires three atoms of a mon-acid base: *e. g.* $3NaO, cPO^5$,—$3ZnO, Fe^2O^3$,—$3MgO^3, Al^2O^3$.

Bi-acid Bases. These contain two atoms of oxygen for each atom of metal: *e. g.* MoO^2, VO^2, SnO^2: in their normal salts, two atoms of a monobasic acid are united with one atom of base: *e. g.* $VO^2, 2SO^3$.

Ter-acid Bases. In these bases, three atoms of oxygen are united with one or two atoms of metal: *e. g.* Al^2O^3, Cr^2O^3, U^2O^3, Fe^2O^3, Bi^2O^3, SbO^3, AsO^3. Their normal salts contain three atoms of monobasic acid united with one atom of base: *e. g.* $Bi^2O^3, 3NO^5$,—$Fe^2O^3, 3SO^3$,—$SbO^3, 3SO^3$.

The 1-, 2-, or 3-acid nature of a base is therefore dependent on the quantity of oxygen which it contains. Each atom of oxygen in the base requires one atom of a monobasic acid; and the ratio between the quantities of oxygen in the acid and the base is a constant quantity. Thus, in the sulphates, the oxygen of the sulphuric acid is always three times as much as that in the base united with that acid to form a normal salt,—whether the base be 1-, 2-, or 3-acid. Similarly in the normal carbonates, *e. g.* KO, CO^2, the quantity of oxygen in the acid is equal to that in the base multiplied by 2; in the nitrates, *e. g.* KO, NO^5, by 5; in the metaphosphates, *e. g.* NaO, aPO^5, by 5; in the pyrophosphates, *e. g.* $2NaO, bPO^5$, by $\frac{5}{2}$; and in the ordinary phosphates, *e. g.* $3NaO, cPO^5$, by $\frac{5}{3}$.

The expression, *Capacity of Saturation* of an acid is used by Berzelius to denote the quantity of oxygen contained in that quantity of base by which 100 parts of the acid are converted into a normal salt. Thus, the capacity of saturation of sulphuric acid is 20; that is to say, 100 parts of that acid take up such a quantity of any given base that the quantity of oxygen contained in it amounts to 20 parts. This number is found by dividing the quantity of oxygen contained in 100 parts of the acid by the number which shows how many times the quantity of oxygen in the base is contained in that belonging to the acid. Thus, 100 parts of sulphuric acid contain sixty parts of oxygen;—and in the sulphates, the acid contains three times as much oxygen as the base; $\frac{60}{3}=20$.

Normal salts are neutral to the taste and to vegetable colours only when they are insoluble, or when the acid and base have about equal power. When the base is powerful, *e. g.* an alkali, and the acid weak, *e. g.* carbonic or boracic acid, the reaction of the alkali predominates: on the other hand, when the acid is relatively stronger, the normal salt exhibits an acid reaction: *e. g.* CuO, SO^3,—$Fe^2O^3, 3SO^3$.

Acid Oxygen-salts. These are formed when one or more atoms of an acid are added to one or more atoms of a normal salt; *e. g.* $KO, 2SO^3$,—$KO, 2CrO^3$,—$KO, 3IO^5$,—$KO, 4TiO^2$. If the acid salts contain water intimately combined, they may likewise be regarded as double salts in which the water plays the part of the second base: thus, $KO, 2SO^3 + HO$ may likewise be written, $KO, SO^3 + HO, SO^3$.

Basic Oxygen-salts. These compounds arise from the combination of one or more atoms of the normal salt with one or more atoms of the base: *e. g.* $2PbO, CrO^3$,—$2PbO, NO^5$,—$3PbO, NO^5$,—$6PbO, NO^5$. These also, when they contain water intimately combined, may be regarded as a species of double salt, or as compounds of the normal salt with

the hydrate of the base, the water in the hydrate playing the part of an acid. Thus, malachite is $2CuO, CO^2 + HO = CuO, CO^2, + CuO, HO$.

Many acid salts exhibit acid re-action; many, however, are neutral or even have an alkaline reaction, if the base be strong and the acid very weak, as in the case of $KO, 2CO^2$, and $NaO, 2BO^3$. Most basic salts are insoluble, and therefore exhibit no particular reaction.

In designating salts according to their stoïchiometrical composition, the names may be formed either according to the number of atoms of acid united with one atom of base, or according to the number of atoms of base united with one atom of acid; hence we have the following nomenclature:—

1 atom of acid to 1 atom of base:—*Simple* or *Mon-acid Salts, e. g.* simple sulphate of potassa $= KO, SO^3$, simple carbonate of soda $= NaO, CO^2$, simple sulphate of alumina $= Al^2O^3, SO^3$, simple phosphate of soda $= NaO, PO^5$.

2 atoms of acid to 1 atom of base: *Bi-acid Salts, e. g.* bichromate of potassa $= KO^2, 2CrO^3$.

3 atoms of acid to 1 atom of base: *Ter-acid Salts, e. g.* teriodate of potassa $= KO, 3IO^5$, tersulphate of alumina $= Al^2O^3, 3SO^3$.

4 atoms of acid to 1 atom of base: *Quadracid Salts: e. g.* quadro-titanate of potassa $= KO, 4TiO^2$.

3 atoms of acid to 2 atoms of base: *Sesqui-acid Salts, e. g.* sesqui-carbonate of soda $= 2NaO, 3CO^2$, which, however, since it cannot be obtained anhydrous, may be regarded as a double salt, viz., $2NaO, 2CO^2 + HO, CO^2$.

1 atom of acid to 2 atoms of base $(= \frac{1}{2} : 1)$: *Di-acid* or *Bibasic Salts, e. g.* dichromate of oxide of lead $= 2PbO, CrO^3$, disulphate of sesqui-oxide of iron $= 2Fe^2O^3, SO^3$, diphosphate of soda (ordinary phosphate of soda) $= 2NaO, cPO^5$ (neglecting the atom of basic water contained in it).

1 atom of acid to 3 atoms of base $(= \frac{1}{3} : 1)$: *Tris-acid* or *Terbasic Salts, e. g.* trinitrate of oxide of lead $= 3PbO, NO^5$, trisulphate of protoxide of mercury $= 3HgO, SO^3$, triphosphate of soda $= 3NaO, cPO^5$.

1 atom of acid to 6 atoms of base $(= \frac{1}{6} : 1)$: *$\frac{1}{6}$-acid* or *Sexbasic Salts, e. g.* $6PbO, NO^5$.

2 atoms of acid to 3 atoms of base $(= \frac{2}{3} : 1)$: *$\frac{2}{3}$-acid* or *Sesquibasic Salts, e. g.* $3Hg^2O, 2NO^5, 3Al^2O^3, 2cPO^5$ (Wavellite).

A few other proportions of the number of atoms of acid and base are likewise occasionally met with.

Generally speaking, simple salts are likewise normal: such, in fact, is always the case when a mon-acid base is associated with a monobasic acid, *e. g.* KO, NO^5, or a ter-acid base with a terbasic acid, *e. g.* Al^2O^3, cPO^5. But when a mon-acid base is combined atom for atom with a bibasic or terbasic acid, *e. g.* NaO, cPO^5, an acid salt is produced, because the acid requires two or three times that quantity of base; and one atom of a monobasic acid with 1 atom of a bi-acid or ter-acid base produces a basic salt, because the single atom of that base requires 2 or 3 atoms of acid in order to produce a normal salt.

(c) *Fluorine-salts.* Combinations of one fluorine-compound with another.

The following are compounds of this kind: KF, HF,—KF, BF^3,—KF, SiF^2,—KF, TiF^2,—$KF, 2ZrF$,—$3NaF, Al^2F^3$.

The fluorine in these compounds takes the place of the oxygen in oxygen-salts: if, therefore, the fluorine contained in them be replaced by

an equal number of atoms of oxygen, the fluorine-salts are converted into oxygen-salts; for instance, KF, BF^3 becomes KO, BO^3, and so forth. The same is true with regard to the following salts; their composition is analogous to that of oxygen-salts, the place of the oxygen being supplied by fluorine, chlorine, bromine, iodine, selenium, or sulphur.

(d) *Chlorine-salts.* Combinations of one chlorine compound with another.

To this group belong: $SnCl^2, 2SCl^2$,—$SbCl^3, 3SCl^2$,—$KCl, HgCl$,—$KCl, 2HgCl$,—$KCl, 4HgCl$ (bi-acid and quadracid chlorine-salts),—$KCl, SnCl^2$,—$KCl, PtCl^2$,—$KCl, AuCl^3$.

(e) *Bromine-salts.* Combinations of one bromine compound with another.

$KBr, PtBr^2$,—$KBr, AuBr^3$.

(f) *Iodine-salts.* Combinations of one iodine compound with another.

KI, AgI,—$KI, 2AgI$ (a bi-acid iodine-salt),—KI, PtI^2,—KI, AuI^3.

(g) *Selenium-salts.* Combinations of two simple selenium-compounds. Selenide of copper and lead $= 2PbSe, CuSe$.

(h) *Sulphur-salts.* Combinations of two simple sulphur compounds.

The electro-negative compound contained in a sulphur-salt is called the *Sulphur-acid;* the electro-positive compound, the sulphur-base. Both art and nature furnish numerous compounds of this class; *e. g.* KS, HS,—KS, CS^2,—KS, HgS,—Grey copper $= Fe^2S^3, Cu^2S$,—Purple copper $= Fe^2S^3, 3Cu^2S$,—Brittle sulphide of silver $= 6AgS, SbS^3$,—Dark red silver $= 3AgS, SbS^3$,—Miargyrite $= AgS, SbS^3$,—Boulangerite $= 3PbS, SbS^3$,—Antimonial Feather-ore $= 2PbS, SbS^3$,—Zinkenite $= PbS, SbS^3$,—Schlippe's salt $= 3NaS, SbS^5$, and the corresponding arsenical compound, $3NaS, AsS^5$.

In the compounds hitherto enumerated—to which perhaps the arsenic-salts and tellurium-salts ought to be added, the electro-negative constituent of the two simple compounds is the one which is common to both. In other, less frequent combinations of the second order, the two simple compounds contain a common electro-positive element, and that element is a metal. To this class belong, particularly, the combinations of a metallic oxide with the chlorine, bromine, iodine, or sulphur compound of the same metal:

Oxychlorides: $3PbO, PbCl^2$,—$5SbO^3, SbCl^3$.

Oxybromides: 5(?) $SbO^3, SbBr^3$,—*Oxiodides,* SbO^3, SbI^3.

Oxysulphides: $SbO^3, 2SbS^3$,—MnO, MnS,—ZnO, ZnS.

With these may likewise be classed the following compounds: SbS^3, SbI^3,—White precipitate $= HgNH^2, HgCl$,—Nickeliferous grey antimony $= NiSb, NiS$;—Arsenical pyrites $= FeAs, FeS^2$,—Cobalt-glance $= CoAs, CoS^2$, &c. &c.

Lastly, we may admit the existence of *Hydrogen-salts,* a class which will include all compounds of ammonia with hydrogen-acids: *e. g.* Sal-ammoniac $= H^3N, HCl$; similarly, H^3N, HS,—H^3N, HI,—H^3N, HBr, &c. If, on the other hand, we suppose that the hydrogen-acid gives up its atom of hydrogen to the ammonia, thereby converting that compound into the quasi-metal, *Ammonium* (NH^4), the formula of sal-ammoniac will become NH^4Cl; it will no longer be hydrochlorate of ammonia, but chloride of ammonium, and must, to a certain extent, be regarded as a compound of the first order. In a similar manner, hydriodate of phosphuretted hydrogen may be regarded either as H^3P, HI, or as PH^4, I.

B. *The two Compounds of the First Order, which unite to form a Compound of the Second Order, have no Common Constituent.*

This case is by far the less common of the two.

Many anhydrous ammonia-compounds belong to this division:

NH^3, CO^2,—NH^3, SO^2,—NH^3, SO^3,—$2NH^3, COCl$,—$5NH^3, PCl^3$,—NH^3, SCl,—NH^3, BF^3,—NH^3, SiF^2,—$NH^3, SiCl^2, NH^3, AsF^3$,—and many other combinations of ammonia with metallic chlorides, bromides, and iodides.

Likewise: $KCl, 2CrO^3$; in this case, KO is replaced by KCl.

Lastly, in this category must be enumerated the *Compounds of Hydrogen-acids with Metallic Oxides*, so far at least as their existence is admitted. Does a metallic fluoride, chloride, bromide, iodide, selenide, sulphide, or telluride, dissolve in water as such? or does it, by taking up the elements of water, become converted into a soluble hydrogen-salt of a metallic oxide? or, what comes to the same thing—does the bringing together of a hydrated hydrogen-acid and a metallic oxide immediately produce water and a compound of the metal with the radical of the hydrogen-acid? or do the metallic oxide and the hydrogen-acid combine together without mutual decomposition? In some cases, the former of these modes of action undoubtedly takes place: hydrated hydrochloric acid and oxide of silver immediately produce insoluble chloride of silver ($AgO + HCl = AgCl + HO$), which, when dried at a gentle heat, is found to be free from oxygen and hydrogen. On the other hand, if aqueous hydrochloric acid be neutralized with soda, the whole remains dissolved, forming a liquid identical with that which is obtained by dissolving common salt (NaCl) in water. Whether this liquid contains in solution NaCl, or NaO, HCl, is a question, which we have no means of deciding. If the solution be evaporated and exposed to a temperature of $-10°$, it yields oblique rhombic prisms of a hydrated salt, which may be regarded either as $NaCl + 4HO$ or as $NaO, HCl + 3HO$: according to the former view, it would be chloride of sodium with four equivalents of water; according to the latter, hydrochlorate of soda with three equivalents of water. If, on the contrary, the saline solution be evaporated at the ordinary, or at a higher temperature, it yields cubical crystals of common salt, NaCl, which are quite free from water, unless, perchance, they contain portions of the mother-liquor (water of decrepitation) enclosed within them. According to the former view, the NaCl merely separates as such from the solution, as the water evaporates: according to the latter view, the O of the NaO combines—as the water in the solution diminishes in quantity—with the H of the HCl, forming water, which likewise evaporates, while the NaCl crystallizes out.

There is no fact yet ascertained by which either of these theories can be positively demonstrated and the other disproved. Nothing more than probable arguments can be alleged in favour of one or the other.

Arguments in favour of the first view—that there are no such things as hydrogen-salts of metallic oxides;

1. The union of two compounds of the first order not containing a common element is, as far as other cases are concerned, of very rare occurrence.

2. It is more simple to conceive the existence of NaCl, &c. as such, in the state of aqueous solution, than to suppose that every such case of solution is accompanied by a decomposition, and every corresponding case

of crystallisation by a recomposition of water. This advantage in point of simplicity is particularly evident in the case of the sulphur-salts. For example: according to the first view, $3NaS, AsS^5$ dissolves in water without change of composition; according to the second, we must assume that the 3Na take 3O from the water, and that the As takes 5O—so that soda and arsenic acid are produced; further, that the 8 atoms of hydrogen thus set free from the water, attach themselves to the $(3+5)$ S, producing hydrosulphuric acid; and thus, $3NaS, AsS^5+8HO$ is converted into $3(NaO, SH) + AsO^5, 5HS$. In this manner a double hydrosulphate would be produced: its composition is, however, liable to the objection that the stronger acid AsO^5, has to play the part of a base, and the weaker, HS, the part of an acid.

3. Many sulphur-salts contain metallic sulphides, the oxides corresponding to which are not known to exist: *e. g.* KS, MoS^4 must, according to the second view, be converted by solution in water into $KO, HS + MoO^4, 4HS$; but MoO^4 is a degree of oxidation of molybdenum not otherwise known.

Arguments in favour of the second view, according to which the combinations of metallic chlorides, &c., with water, contain hydrogen-salts of metallic oxides.

1. Water is in all other cases most inclined to dissolve those compounds which contain one of its constituents: thus it dissolves acids, alkalis, oxygen-salts, &c. Hence it is probable that water would not dissolve metallic sulphides, &c., if these compounds did not previously take up the elements of water.

2. No simple metal is soluble in water: thence it appears remarkable, according to the first view, that telluride of potassium, an alloy of two metals, should dissolve in water; but the act of solution becomes easily intelligible, if we suppose the potassium previously converted into KO, and the tellurium into H Te.

3. Phosphide of potassium in contact with water gives rise to phosphuretted hydrogen gas, which escapes, and oxide of potassium, which remains dissolved in the water: why should not sulphide of potassium, in contact with water, produce KO and HS^5? The cases appear precisely analogous; in both of them, the great affinity of potassium for oxygen, and of phosphorus or sulphur for hydrogen, must give rise to decomposition of the water; the only difference being that the hydrosulphuric acid produced in the latter case remains in combination with the potassa, whereas the phosphuretted hydrogen, for which potassa has no affinity, is evolved in the form of gas.

4. Oxygen is considered to be more electro-negative than chlorine; nevertheless, KO dissolved in water has a strong alkaline reaction, whereas K Cl is neutral. This apparent anomaly disappears if we suppose KO and H Cl to be formed, the latter of which compounds, being a strong acid, completely neutralizes the potassa. KS dissolved in water exerts an alkaline reaction, because HS is a much weaker acid than H Cl. And generally, the reaction of K Cl, K I, KS, &c., in the state of aqueous solution, stands in direct relation to the strength of the hydrogen acid produced in the act of solution.

5. Chloride of bismuth, in contact with water, is resolved into precipitated oxide of bismuth, retaining a small quantity of chloride, and hydrated hydrochloric acid, in which a small quantity of oxide of bismuth remains dissolved. Here it is plainly seen that metallic chlorides in contact with

water produce hydrogen salts of metallic oxides, which, according to the nature of the metal, either remain dissolved in the water, or are resolved into a basic and an acid salt—just like the corresponding nitrates.

6. When a solution of magnesia or alumina in dilute hydrochloric is evaporated to complete dryness, there remains, not $MgCl$ or Al^2Cl^3, but MgO or Al^2O^3, while the hydrochloric acid evaporates with the water. This fact is easily explained upon the second hypothesis. The hydrochloric acid having but a feeble affinity for these earths escapes, the separation being induced partly by its attraction for heat, partly by its attraction for water. But, according to the first hypothesis, it must be assumed that, at a certain degree of concentration, the $MgCl$ or Al^2Cl^3 interchanges elements with the water still remaining, the products being MgO or Al^2O^3 which remains, and HCl, which escapes.

7. The aqueous solution of protochloride, protiodide, &c., of iron exhibits the same reactions as the compounds of the protoxide of iron with oxygen-acids: when, therefore, we speak of the reactions of the salts of protoxide of iron, we must understand by this expression, not only the compounds of protoxide of iron with oxygen-acids, but likewise the aqueous solutions of protochloride of iron, &c., although the latter, according to the first hypothesis, do not contain protoxide of iron. Here, then, we either introduce an ambiguity by tacitly supposing, as is commonly done, that the expression "*salt of protoxide of iron,*" likewise extends to solutions of the protochloride, &c., or else we must in every case explicitly declare that we are speaking not only of salts of the protoxide of iron, but likewise of the aqueous solutions of the compounds of iron with one atom of fluorine, chlorine, bromine, iodine, &c. Similarly with regard to the other metals*.

8. The aqueous solution of nitrate of cobalt is red, so is that of the chloride; but the former solution when evaporated to dryness leaves a red residue, the latter, a blue one,—because the oxygen-salt, after parting with its water, still remains a salt; whereas dissolved hydrochlorate of the oxide of cobalt is converted on evaporation into a non-saline body, the chloride of cobalt. Similarly, with chloride of chromium.

The most probable view of the matter appears to be that when a metallic chloride, &c. is brought in contact with water, the opposing affinities are either exactly or nearly in equilibrium. In the case of $NaCl$, for example, the affinity of Na for Cl + that of O for H must be considered as about equal to the affinity of Na for O + that of Cl for H + that of NaO for HCl. If the former sum were the greater, the $NaCl$ would dissolve as such in the water; if, on the contrary, the latter sum were the greater, the compound actually dissolved would be NaO, HCl. Since, however, the two sums appear to equilibrate each other, we may be allowed to regard a metallic chloride, &c. dissolved in water in the

* In translating this paragraph, it was necessary to adhere strictly to the forms of expression adopted by the author; otherwise the meaning would have been lost. It must, however, be observed that the ambiguity spoken of arises from the use of the particular expression "*salts of protoxide of iron*" (*Eisenoxydul-salze*); but if we adopt the mode of expression more usual in English, viz., "*protosalts of iron,*" the ambiguity is done away with; for this expression is at once understood to apply to the protochloride, protiodide, &c., as well to salts of the protoxide properly so called. Neither is there any confusion (notwithstanding the slight dissimilarity) in explaining the action of different reagents on the several solutions. For instance, in the action of potassa on a solution of the protsulphate we have: FeO, SO^3 and KO yield FeO and KO, SO^3; and in the case of the protochloride, $FeCl$ and KO yield FeO and KCl. [W.]

one way or the other, according to the greater facility of explanation which either hypothesis may present. For example, in considering the precipitation of $CaCl$ dissolved in water by KO, CO^2, it is easier to adopt the second hypothesis and explain the reaction as a decomposition by double affinity, whereby CaO, HCl and KO, CO^2 are converted into CaO, CO^2, and KO, HCl—than to suppose, according to the first hypothesis, that $CaCl$ and KO yield, also by double affinity, the new compounds CaO and KCl, and then that the CO^2 previously combined with the KO is transferred to the CaO. But in many other cases, *e. g.* in that of the sulphur-salts and the theory of the preparation of kermes-mineral, the first mentioned hypothesis gives by far the simpler explanations.

The former theory is that of Berzelius, who first reduced it to a complete form, and by the discovery of the sulphur-salts gave it important support. Among the advocates of the latter theory are: R. Phillips (*Ann. Phil.* 17, 27); Schnaubert (*J. pr. Chem.* 6, 353.)

III. *Compounds of the Third Order.*

1. Combinations of a Compound of the Second Order with a Compound of the First.

A. Combinations of simple Oxygen, Fluorine, Chlorine, Bromine, Sodine, Selenium, and Sulphur-salts with water: *e. g.* Gypsum, $CaO, SO^2 + HO$. [Vid. *Water*, in the chapter on *Hydrogen.*]

B. Combinations of simple Oxygen-salts with Ammonia: *e. g.* $AgO, NO^5 + 3NH^3$. [Vid. *Ammonia*, in the chapter on *Nitrogen.*]

C. Certain other cases belonging to this head: Matlockite, $PbO, CO^2 + PbCl$,—Pyromorphite, $3(3PbO, PO^5) + PbCl$,—$3(KCl, HgCl) + CuCl$,—$HgNH^2, HgCl + 2HgO$.

2. Combinations of two Compounds of the Second Order one with the other.

Double Salts in the most extended sense.

A. The two simple salts which combine together contain the same acid. This case is the most frequent, and yields the ordinary *Double* or *Triple salts*. It appears that only normal salts (pp. 6....8) are capable of forming double salts.

Double Oxygen-salts: $KO, SO^3 + ZnO, SO^3$,—anhydrous Alum $= KO, SO^3 + Al^2O^3, 3SO^3$.

In this class may likewise be included those compounds in which water plays the part of one of the bases, *e. g* .$KO, SO^3 + HO, SO^3$. Since, however, KO, SO^3 when mixed with HO, SO^3 gives rise to considerable evolution of heat, which is due to the combination of KO, SO^3 with SO^3, Hess (*Pogg.* 52, 110) gives preference to the formula, $KO, 2SO^3 + HO$, according to case iii, i. A.

Polybasic acids may combine with several bases at once without producing a double salt properly so called. Thus, an atom of ordinary phosphoric acid requires three atoms of base (metallic oxide or water) to saturate it, and these three atoms of base may be of one, two, or three different kinds; *e. g.* $3NaO, cPO^4$,—$(2NaO, HO) + cPO^5$—$(KO, NaO, HO) + cPO^5$.

The two bases of a real double salt are never isomorphous, (thus in the examples above given, KO is not isomorphous either with ZnO or

with Al^2O^3); but phosphoric acid may simultaneously take up several isomorphous bases, as KO and NaO. In real double salts, each atom of base has its own atom of acid or several; so that the formula divides itself into two parts, each of which is the expression of a simple salt: but in those salts of phosphoric acid which contain several bases together, such a division cannot be made, because the different bases belong altogether to the same atom of acid. (Graham, *Phil. Mag. J.* 13, 319; also *J. pr. Chem.* 15, 437.)

Double Sulphur-salts. Bournonite: $(3CuS, SbS^3) + 2\,(3PbS, SbS^3.)$

Undoubtedly there also exists double fluorine, chlorine, bromine, iodine, selenium, and tellurium-salts.

B. The two simple salts contain the same acid. This case is of rarer occurrence. Copper-salammoniac; $NH^3, CuO + NH^4O, SO^3$.—Similarly, $PbO, CO^2 + PbO, SO^3$.

IV. *Compounds of the Fourth Order.*

To this class belong especially the compounds of double salts with water, *e. g.* Crystallized alum: $(KO, SO^3 + Al^2O^3, 3SO^3) + 24HO$.

V. *Compounds of the Fifth Order.*

Under this head may perhaps be included the solutions of crystallized alum and other compounds of the fourth order in water and other liquids: definite compounds of this order do not however appear to exist.

Remarks upon the Theory of Salts.

The idea of a *salt* has, with the progress of chemistry, undergone numerous alterations.

1. In former times, the term *salt* was applied to various bodies whose principal characteristics were solubility in water, a peculiar taste, and generally also the capability of crystallizing: and these bodies were divided into *Acid salts* (the oxygen and hydrogen-acids of the present day); *Alkaline salts* (the substances now called alkalis); *Neutral salts* (those compounds of acids and alkalis which are soluble in water); *Medium salts* (compounds of the earths with acids); and *Metallic salts* (compounds of the heavy metallic oxides with acids). Insoluble compounds of alkalis, earths, and heavy metallic oxides with acids, such as calcspar and sulphate of lead, were classed, not with salts, but with the earths and metallic calxes: on the other hand, sugar was called a vegetable salt.

2. Since the introduction of the antiphlogistic theory, all compounds of salifiable bases with acids have been reckoned as salts,—the term *base*, was however originally restricted to the salifiable metallic oxides and ammonia, and the term *acid* to those which are now denominated oxygen and hydrogen acids.

3. On more exact investigation of the relation of hydrogen-acids to metallic oxides, it was found that, according to the idea of a salt laid down in (2), common salt, notwithstanding that it was the substance to which the name of salt was first applied, could no longer be regarded as a salt, since in the crystalline state it is $NaCl$, a compound of the first order, not containing either base or acid; and generally, that all compounds of hydrogen-acids with metallic oxides are, when reduced to the anhydrous state, no longer combinations of an acid with a salifiable base. Since, however, the metallic fluorides, chlorides, bromides, &c., exhibit a close resem-

blance to the oxygen-salts, the three following methods, described under the heads 4, 5, and 6, have been devised to account for this resemblance.

4. It is supposed that common salt, when in the dry state, is not really a salt, but that when dissolved in water, it is converted into the true saline compound, hydrochlorate of soda; and similarly, that all other metallic chlorides, fluorides, bromides, and iodides, when dissolved in water, are to be regarded as hydrogen-salts of metallic oxides. This view has already been explained (pp. 11 .... 13).

5. Berzelius distinguishes two classes of salts: *Amphid salts* and *Haloid salts*.

The class of *Amphid salts* comprises, according to Berzelius, the oxygen-salts (p. 5), sulphur-salts (p. 9), selenium-salts, and tellurium-salts. With reference to these compounds, Berzelius calls the elements, oxygen, sulphur, selenium, and tellurium, by the name of *Corpora amphigenia, Amphigenous bodies*, that is to say, producers both of acids and of bases. (The fluorine-salts, (p. 8), chlorine-salts, (p. 9), bromine-salts, (p. 9), and iodine-salts may likewise, according to Bonsdorff, Boullay, and others, be included in the same category, inasmuch as they are all compounds of the second order. Berzelius considers them as double haloid salts.)

The *Haloid salts* are compounds of fluorine, chlorine, bromine, iodine, and cyanogen, with metals; the bodies just enumerated are called by Berzelius, *Salifiers, corpora halogenia*. When to any such haloid salt there is added the hydrogen-acid of the corresponding salifier, an *acid haloid salt* is produced, *e. g.* KF, HF. If, on the other hand, a haloid salt be mixed with the oxide of the metal which it contains, a *basic haloid salt* is the result, *e. g.* $SbO^3, SbCl^3$. Finally, when one haloid salt combines with another containing either the same salifier or the same metal as the former, the resulting compound is a *double haloid salt* (the compounds already spoken of on *page* 9, as fluorine, chlorine, bromine, and iodine-salts).

Although common salt is called a haloid salt, it nevertheless remains a compound of the first order, and consequently separated by as great a gulf as before from the amphid salts, which are compounds of the second order. If, again, the term salt be likewise extended to compounds of the first order, exact definition of it is becomes impracticable. Moreover, if KCy be considered a haloid salt, why should not KS, KSe, and KTe be regarded in the same light? On the whole, it appears more appropriate, as pointed out by Bonsdorff (*Pogg.* 17, 115 and 247; 19, 336), to include the double haloid salts in the class of amphid salts under the names of fluorine, chlorine, bromine, and iodine-salts.

6. *Binary Theory of Salts.*—Sir H. Davy (*Gilb.* 54, 377) first threw out the suggestion that chlorate of potassa is not KO, ClO^5, but K, ClO^6; nitrate of potassa, not KO, NO^5, but K, NO^6. Dulong (*Mém. de l'Institut*, ann. 1813 .... 15, p. cxcix; abstr. *Schw.* 17, 230) put forth the same hypothesis with reference to the sulphates and oxalates; and Clark (*Ann. Pharm.* 27, 160), Graham (*Elements*, pp. 160—166), Liebig (*Ann. Pharm.* 26, 170), and Daniell (*Ann. Pharm.* 36, 32), have endeavoured to generalize and support this theory. Anhydrous hydrogen-acids redden litmus, anhydrous oxygen-acids do not. It is not till water is added to them that the latter acquire the property of reddening litmus. It appears therefore, that it is the water which converts them into acids, and, in fact, into hydrogen-acids. Thus, anhydrous sulphuric acid, SO^3, in contact with an atom of water, does not become HO, SO^3, but the SO^3 takes from the water an atom of oxygen and forms SO^4, which then combines

with the hydrogen of the water, producing a hydrogen-acid, H, SO^4. When H, SO^4 (oil of vitriol) comes in contact with KO, the O of the KO combines with the H of the acid, forming water, and K, SO^4 is produced. In contact with potassium, H, SO^4 is resolved into H, which escapes, and K, SO^4. The chemical relations of H, SO^4 are therefore precisely similar to those of HCl, the only difference between these two acids being that the radical Cl of HCl is simple, while the radical SO^4 of the acid H, SO^4 is compound. This theory may likewise be extended to the other oxygen-acids and salts: for example, nitre, according to this view, is K, NO^6, &c. &c. Particular names are required for the compound radicals: SO^4 is called by Daniell, *Oxysulfion;* by Graham, *Sulfatoxygen;* by Otto, *Sulfan,* and its compounds with hydrogen or with metals, *Sulfanides;*—NO^6 is called by Daniell, *Oxynitrion;* by Graham, *Nitratoxygen;* by Otto, *Nitran.* Similar names are applied to the remaining radicals. Graham assigns to these compound radicals the common name of *Salt-radical,* and to the metal, hydrogen, or ammonium therewith combined, the name of the *Basyle.*

The binary theory is recommended by the following considerations:—

1. It resolves the amphid salts into compounds of the first order, and thereby renders them precisely analogous to the inorganic haloid salts, with the sole difference that the former contain a compound, the latter a simple radical. The relations of the metals and metallic oxides towards the hydrates and the oxygen-acids and towards the anhydrous hydrogen-acids become identical. Zn evolves the same quantity of hydrogen gas with HCl as with H, SO^4, producing $ZnCl$ in the first instance, and Zn, SO^4 in the second. Lime $= CaO$ produces equal quantities of water with HCl and with H, SO^4,—and this water is in both cases formed by the union of the oxygen of the lime with the hydrogen of the acid; whereas, according to the ordinary view, the water which CaO yields in contact with HCl is a product,—but that which is obtained from CaO and HO, SO^3 existed previously, and is, therefore, an educt.

2. The decomposition of oxygen-salts by the electric current is more easily explained on the binary theory than on the other. (*Comp.* Daniell, vol. i. p. 459.)

3. The binary theory of salts accounts, to a certain extent, for the three isomeric conditions of phosphoric acid. Hydrated metaphosphoric acid, $HO, a\,PO^5$, which takes up but one atom of base, is H, PO^6, and the single atom of hydrogen may be replaced by one atom of metal. Hydrated pyrophosphoric acid, $2HO, b\,PO^5$ is $2H, PO^7$; and by virtue of the two atoms of hydrogen which it contains, it decomposes 2 atoms of metallic oxide, *e. g.* NaO, producing $2HO$ and $2Na, PO^7$. Lastly, the hydrate of ordinary phosphoric acid, $3HO, c\,PO^5$ is to be regarded as $3H, PO^8$; in contact with $3NaO$ it yields $3HO$ and $3Na, PO^8$. According to this theory, then, the difference between the three acids consists in this, that they contain different salt-radicals, viz., PO^6, PO^7, and PO^8, the first of which takes up one, the second two, and the third three atoms of metal.

4. The theory explains why an atom of a base requires as many atoms of an acid to produce a normal salt, as the base itself contains atoms of oxygen; viz., because each atom of oxygen in the base combines with one atom of hydrogen in the acid. As many atoms of salt-radical as are thus set free, so many go over to the metal. This will be seen by reference to the following tabular example:—

	Ordinary Formula.	Sulfan Formula.	Corresponding Chloride.
Sulphate of dinoxide of mercury ..	Hg^2O, SO^3	$= 2Hg, SO^4$	.... $2Hg, Cl$
Protosulphate of iron............	FeO, SO^3	$= Fe, SO^4$	.... Fe, Cl
Persulphate of iron..............	$Fe^2O, 3SO^3$	$= 2Fe, 3SO^4$	.... $2Fe, 3Cl$
Persulphate of tin	$SnO^2, 2SO^3$	$= Sn, 2SO^4$	.... $Sn, 2Cl$

5. The decompositions of oxygen-salts by haloid salts are directly explained on this theory as decompositions by double affinity, *e. g.* that of sulphate of potassa by chloride of barium: $Ba, Cl + K, SO^4 = Ba, SO^4 + KCl$.

6. This theory likewise explains the isomorphism of sulphate of soda and hypermanganate of baryta. (Clark, vol. I. p. 92.)

7. Schröder finds that the Binary Theory of Salts is more in accordance with his Theory of Volumes than the ordinary theory*.

[See also Wilson, *Quart. Journ. Chem. Soc.*, 1, 332.]

The objections to the Binary Theory of Salts are as follows:

1. It assumes the existence of many compounds which are not known to exist in the separate state, viz. $SO^4, NO^6, PO^6, PO^7, PO^8$, &c., and thus encumbers chemical science with a mass of hypothetical substances†.

2. All oxygen-acids do not form with the first atom of water, compounds which can be properly regarded as combinations of hydrogen with a salt-radical. Thus, in the case of carbonic acid, chromic acid, &c., we know of no hydrate which can be looked upon as H, CO^3, or as H, CrO^4. In such cases, therefore, the compound of the salt-radical with hydrogen must be hypothetical, as well as the salt-radical itself.

3. It is not easy to see where the limits of this binary theory are to be placed. Unless it is to be extended to *all* oxygen-salts, it fails to confer the promised advantage of uniting the amphid and haloid salts in one single class of similarly constituted compounds. If, again, the theory be extended—as consistency requires—to all salts, then not only must silicate of soda, NaO, SiO^2, be regarded as Na, SiO^3—and similarly with the salts of the weakest acids—but likewise Spinell, $3MgO, Al^2O^3$, must be considered as $3Mg, Al^2, O^6$,—hydrate of potassa KO, HO, as K, HO^2;—in short, the theory must be extended to all compounds hitherto considered to be of the second order, whereby a vast number of hypothetical compounds will be unnecessarily created, and great confusion introduced into chemical nomenclature. Besides, if it be allowed to alter the formulæ of simple salts in this manner, the same changes may with equal propriety be made in those of the double salts. For instance, $KO, SO^3 + ZnO, SO^3$ may be written: $K + Zn, 2SO^4$, the result being a compound of K, with a salt-radical which differs from other salt-radicals only in containing an additional element. But that this formula is not the correct expression of the mode of combination of the elements of the double salt, will in all probability be generally admitted; but there is likewise some reason for believing that the composition of simple sulphate of potassa is more correctly expressed by KO, SO^3 than by K, SO^4.

4. Graham himself (*Lehrb.* 2, 147) draws attention to the doubtful explanation which this theory gives of the fact that one atom of potassa

* Filhol has shown that the superiority of the binary theory in this respect is only apparent.—(See Vol. I. p. 81.) [W.]

† The ordinary theory is liable to the same objection, though not to an equal extent; as far as actual separation is concerned, NO^5 is in the same predicament as NO^6; and the same is the case with many other acids, oxalic and acetic acid for example. [W.]

can combine either with one or with two atoms of sulphuric acid; thus—(a) $KO, SO^3 = K, SO^4$; (b) $KO, 2SO^3 = K, S^2O^7$. For these two salts we are obliged then to admit the existence of two different salt-radicals. So likewise one atom of potassa combines with 1, 2, and 3 atoms of chromic acid, and accordingly, the binary theory requires us to admit the existence of three different radicals, viz. CrO^4, Cr^2O^7, and Cr^3O^{10}.

5. According to the binary theory, the class of acids must be supposed to include all hydrogen compounds which, in contact with metallic oxides, produce water and a compound of the radical with the metal,—as for example, HCl and NaO yield HO and $NaCl$, and similarly $3H, PO^8$ and $3NaO$ yield $3HO$ and Na^3, PO^8. But if this be admitted, then not only must phosphuretted hydrogen and arseniuretted hydrogen (H^3P and H^3As) be regarded as terbasic acids—since H^3P and $3CuO$ yield $3HO$ and Cu^3P—but even ammonia, H^3N, which with many metallic oxides yields products of double decomposition (*e. g.* H^3N and $3HgO$ yield $3HO$ and Hg^3H), must be regarded in the same light.

6. The assumption that potassium and other metals possessing great affinity for oxygen can remain in union with SO^4, NO^6, &c., without decomposing them, is improbable: and if we moreover consider hydrate of potassa as consisting of K, HO^2, instead of KO, HO, we must admit that even peroxide of hydrogen can remain in contact with potassium without suffering decomposition. All this implies the existence of enormously powerful affinities between K and SO^4, NO^6, &c., to overpower the affinity of K for O.

7. It is commonly stated as a difference between inorganic and organic acids, that the former contain a simple, the latter a compound radical. If the binary theory be adopted, this difference must vanish.

8. The objections of Hess, founded upon the theory of Heat, will be found in *Poggendorff's Annals*, 53, 499. Persoz likewise adduces several arguments against it. (*Chim. molecul.* 815.)

The advocates of the binary theory have doubtless been aware of these various objections: at all events, this theory has never been completely carried out in detail.

Subdivision I.

NON-METALLIC ELEMENTARY BODIES.

The Non-metallic Elements, called by Berzelius, Metalloids, are, at ordinary pressures and temperatures, either gaseous: Oxygen, Hydrogen, Nitrogen, Chlorine, and doubtless also Fluorine; or liquid: Bromine; or solid: Carbon, Boron, Phosphorus, Sulphur, Selenium, and Iodine. Those which are solid are either transparent: Carbon, Phosphorus, Sulphur; or very feebly translucent, and at the same time possessed of the metallic lustre: Selenium, Iodine; or opaque: Boron (which substance has hitherto been obtained only in the pulverulent state). All those which assume the liquid or solid state are non-conductors of electricity.

According to their chemical relations, they may be divided into:

1. Electro-negative elements, *Oxygenoids, Chloroids,* or *Supporters of*

Combustion; Oxygen, Fluorine, Chlorine, Bromine, Iodine, Selenium, and Sulphur.

2. Electro-positive elements, *Combustibles* or *Metalloids in the more restricted sense;* Phosphorus, Boron, Carbon, Hydrogen.

3. Nitrogen, from its peculiar characters, stands alone.

CHAPTER I.

OXYGEN.

Priestley. *Experiments and Observations on different kinds of air.* London, 1775 ...1777. 2, 29; 3, 1.

Priestley. *Experiments and Observations relating to various branches of Natural Philosophy.* London, 1779. 1, 92.

Scheele. *Abhandlung von der Luft und dem Feuer.* Upsala and Leipzig, 1777.

——— New Observations. *Crell. Ann.* 1785. 2, 229 and 291.

Lavoisier's Memoirs. *Crell. Chem. J.* 4, 140; 5, 125.—*Crell. Chem. Ann.* 1786. 1, 33 and 136; 1788. 1, 354, 441, 528, 550 and 552; 2, 55, 262, 431 and 433; 1789. 1, 145, 162, 260 and 323; 2, 68, 145 and 433; 1790. 1, 69 and 518;—1791. 1, 71.

——— *System der antiphlogistischen Chemie, übers. von Hermbstädt,* 1803. 1. 29 . . . 122.

Berzelius. Electro-chemical Theory of Combustion. *Schw.* 6, 119.

——— *Lehrbuch der Chemie,* Aufl. 3. B. 5, S. 46.

Grotthuss, on Combustion. *Gilb.* 33, 212.—*Schw.* 4, 238.—*Gilb.* 58, 345.—*Gilb.* 69, 241.

H. Davy, on Flame, *Phil. Trans.* 1817. 45 and 77; also *Schw.* 20, 134 and 175; also *Gilb.* 56, 113 and 225.

Walden, on Flame. *Phil. Mag. J.* 13, 86; also *J. pr. Chem.* 15, 223.

On Combustion by Platinum, &c.: Erman, *Abhandlungen der Akademie der Wissenchaften in Berlin für* 1818 and 1819. S. 368.—Döbereiner. *Schw.* 34, 91;—38, 321 (also *Gilb.* 74, 269); *Schw.* 39, 159—42, 60;—63, 465;—*Kastn. Archiv.* 2, 225.—Further, *Ueber neuentdeckte und höchst merkwürdige Eigenschaften des Platins,* u. s. w. Jena, 1823.—Dulong & Thénard, *Ann. Chim. Phys.* 23. 440; also *Gilb.* 76, 83.—*Ann. Chim. Phys.* 24, 380: also *Schw.* 40, 229; *Gilb.* 76, 89; *Kastn. Archiv.* 1, 81.—Pleischl, *Schw.* 39, 142, 201 and 351 (the latter also in *Gilb.* 76, 98); *Repert.* 17, 97.—C. G. Gmelin, *Schw.* 28, 515.—Pfaff. *Schw.* 40, 1.—Dana, *Sill. Am. J.* 8, 198; also *Schw.* 43, 380.—Schweigger. *Schw.* 39, 223;—40, 10 and 237.—Karmarsch. *Gilb.* 75. 80.—Chladni, *Gilb.* 61, 346;—75, 98.—Stratingh. *Repert.* 21, 410.—Van Dyk, *Repert.* 21, 235.—Wöhler. *Berzelius* 4ter *Jahresbericht.* 69.—Turner, *Ed. Phil. J.* 11, 99; 12, 311; the beginning also in *Pogg.* 2, 10,—W. Henry, *Ann. Phil.* 21, 364; 25, 416.—W. Charles Henry, *Phil. Mag. J.* 6, 354; also *J. pr. Chem.* 5, 109; abstr. *Pogg.* 36, 150.—*Phil. Mag. J.* 9, 324; also *Pogg.* 39, 385; also *J. pr. Chem.* 9, 347.—Graham, *N. Quart. J. of Sc.* 6, 354.—Faraday, *Experimental Researches in Electricity,* 1, 165; also *Phil. Trans.* 1834, I. 1; also *Pogg.* 33, 149.

* The terms electro-negative and electro-positive must be understood as merely relative. [W.]

De la Rive & Marcet, *Ann. Chim. Phys.* 39, 328.—De la Rive, *Pogg.* 46, 489 and 492; *Pogg.* 54, 386 and 397.

Acidifying Principle, Oxygène, Oxygenium, Sauerstoff (Lavoisier); and in the state of gas; *Oxygen Gas, Vital Air* (Condorcet), *Pure Air, Feuerluft* (Scheele), *Dephlogisticated Air* (Priestley), *Gas Oxygène, Gas Oxygenium, Sauerstoff-gas.*

History. The older chemists regarded atmospheric air as a simple substance: Scheele and Priestley discovered that it consists of two distinct kinds of air, one only of which is capable of supporting the life of animals and the combustion of inflammable bodies. The actual separation of this portion of the air, which is essential to combustion and respiration, was effected by Priestley in 1774, and by Scheele (to whom Priestley's discovery was then unknown) in 1775. Immediately afterwards, Lavoisier showed that combustion consists in the combination of the burning body with oxygen contained in oxygen gas. He likewise made this discovery the groundwork of a simple *Theory of Combustion*, the *Antiphlogistic Theory*, whereby the *Phlogistic Theory* of Becher and Stahl, which supposed that combustible bodies in the act of burning do not take any thing up, but on the contrary, evolve a hypothetical substance, called *Phlogiston*,—a theory which had been received as true for about a century,—was completely overthrown. Grotthuss, and more especially Sir H. Davy, added to the existing knowledge of the nature of the combustion process, particularly as regards flame. E. Davy's discovery of a preparation of platinum which excites the combustion of alcohol at ordinary temperatures—and a similar observation of Erman—led Döbereiner to the discovery, that finely divided platinum induces the combustion of certain gaseous bodies at ordinary temperatures.

Sources. Oxygen is the most abundant of all known substances. It constitutes at least one-third of the solid mass of the earth, which, so far as we are acquainted with it, is mainly composed of metallic oxides and oxygen-salts. Water contains 0·89, and atmospheric air 0·23 of its weight of this substance: it is likewise found in most organic compounds.

Preparation. 1. By heating chlorate of potassa to low redness.—In this action, KO, ClO^5, is converted, by parting with six atoms of oxygen (39 per cent), into KCl. The salt is heated over charcoal or alcohol in a glass retort connected with a gas-delivery tube (*App.* 34). According to Bucholz (*Schw.* 6, 219), the retort should not be filled to more than $\frac{1}{10}$ of its bulk, because the salt on fusing swells up with violence: hence also the heat must be cautiously applied. Gay-Lussac and Humboldt moisten the salt slightly with water, in order that the vapour evolved at the beginning of the operation may expel the air of the vessel. The gas obtained from chlorate of potassa is purer than that from any other source.

¶ The decomposition of the chlorate of potassa is greatly facilitated by mixing it with a small quantity of black oxide of manganese in fine powder: a very moderate heat is then sufficient for the evolution of the gas. The oxide of manganese undergoes no change, but appears to act only by catalysis. This is the most convenient of all methods of preparing oxygen. The gas which it yields cannot, however, be so implicitly depended upon for purity as that which is obtained by the use of chlorate of potash alone: for the manganese is often mixed with particles

of carbonaceous matter; and these become oxidized by the free oxygen, and converted into carbonic acid. But when absolute purity is not an object, and the quantity of gas required not very large, this method is greatly to be preferred to all others. ¶

2. By ignition of red oxide of mercury.—HgO, when heated to redness, is resolved into vapour of mercury, which condenses in the colder part of the apparatus, and oxygen gas (8 p. c.), which escapes. On account of the higher temperature required for this decomposition, it is advisable to coat the retort (*App.* 34) with clay previously mixed with cow-hair. The oxygen gas thus obtained may be contaminated with vapour of hyponitric acid, if the oxide of mercury is not quite free from nitric acid.

3. By strong ignition of pounded *manganese* (Braunstein).—The term *manganese* is commonly applied to several native oxides of the metal of that name. The one which is best adapted for the preparation of oxygen gas is *Pyrolusite*, MnO^2. Three atoms of this substance, containing Mn^3O^6, are resolved by heat into Mn^3O^4 and O^2 (12·3 per cent), which escapes. Pyrolusite is crystalline, and yields a grey powder. *Manganite*, Mn^2O^3, HO, crystallizes in the same manner, but gives a brown powder. Three atoms of it, $= Mn^6O^9$, 3HO are resolved into Mn^6O^8 and one atom of oxygen (therefore only 3 p. c.), which escapes with the aqueous vapour. *Braunite* or *Hartmangan*, Mn^2O^3, is amorphous, dense, and hard: 3 atoms $= Mn^6O^9$ yield Mn^6O^8 and one atom (3·4 p. c.) of oxygen gas.—The quantity of gas actually obtained is always smaller than the calculated quantity, because the manganese is mixed with foreign substances. Carbonate of lime is a frequent impurity, and hence the gas is often contaminated with carbonic acid. Many kinds of manganese, especially braunite, likewise contain carbon, which combines with oxygen at the commencement of the ignition, and forms carbonic acid, which is evolved. The oxygen gas must therefore be agitated with milk of lime to free it from carbonic acid. The most convenient vessel for igniting the manganese is a bottle of cast or wrought iron (*App.* 35), which may be nearly filled with the pounded* manganese. To the mouth of the bottle is adapted an iron tube, which should be smeared with loam, driven tight into the bottle, and cemented on the outside with plaster of Paris. To prevent the gypsum from falling off from the effect of the heat, the iron tube should be covered with blotting-paper as far down as the gypsum, and water continually dropped upon it by means of a dropping-bottle (*App.* 36).† For small quantities of gas, a gun-barrel welded together at bottom, and connected with a gas-delivery tube, may be used (*App.* 37). Coated glass retorts of moderate size may likewise be employed (*App.* 34); but they must be heated very gradually. Earthen retorts are utterly useless; for some of them are porous even in the cold,—as may be shown by immersing them in water and blowing air into them—others become so at a red heat. Hence oxygen gas escapes through the pores, while carbonic acid and nitrogen enter to supply its place. (Vol. I., page 24.)

4. By heating manganese with an equal weight of oil of vitriol.—When manganese is heated alone, it is converted into Mn^3O^4; but when it

* It is much better to have the manganese in small lumps: the powder frequently swells up, especially if it be not absolutely dry, completely filling the bottle and gas-delivery tube, and a considerable quantity of it is ejected at the end of the tube, causing great inconvenience. [W.]

† All this trouble may be saved by using a well fitting tube. [W.]

is heated in contact with sulphuric acid, the product is MnO, SO^3: in the latter case, therefore, the quantity of oxygen evolved is greater than in the former. Pyrolusite, MnO^2, treated in this manner with HO, SO^3 yields, besides vapour of water, one atom (18·3 p.c.) of oxygen gas. (*Sch.* 16, Vol. I.) One atom of manganite, Mn^2O^3, HO, yields one atom (9 p.c.); and one atom of braunite, Mn^2O^3, yields one atom (10 p.c.) of oxygen gas. The first portions of gas evolved often contain chlorine, partly because the manganese is frequently contaminated with chloride of calcium, partly because the sulphuric acid often contains hydrochloric acid (A. Vogel, *J. pr. Chem.* 1, 446). The chlorine may be absorbed by passing the gas through water, or more quickly, through milk of lime. The most convenient vessel for the operation is an uncoated glass retort (*App.* 34). The manganese is put in first, and then the oil of vitriol, the materials filling up, at most, one half of the retort. The powder must be well mixed up with the acid before the heat is applied. The retort is then placed upon a tripod, and adjusted in the upper part of the air-furnace; and the fire, as well as the draught, is very gradually increased till the bottom of the retort is brought to a low red heat. The retort almost always cracks before the decomposition is complete, in consequence of the sulphate of manganese being deposited in the solid state at the bottom, and probably expanding more quickly than the glass: for this reason, the method is not so economical as it appears to be by calculation.* Iron vessels cannot be used in this process.

5. By ignition of nitrate of potassa.—This salt, KO, NO^5, when heated above its melting point, is first converted, by the loss of two atoms of oxygen (= 15 per cent.), into nitrite of potassa, KO, NO^3,—and this, when raised to a still higher temperature, is likewise decomposed, evolving a mixture of nitrogen and oxygen gases. The portions which are nearest to the sides of the vessel become most strongly heated, and are therefore most rapidly decomposed; particularly as the silica of the containing vessel takes up potassa from the nitre, and drives out the whole of the nitric acid in the form of nitrogen and oxygen gas. From this cause, the oxygen gas obtained from nitre is contaminated with nitrogen, even from the beginning of the operation: moreover, the quantity of nitrogen continually increases as the action proceeds, so that the gas obtained is quite unfit for exact experiments. The operation may be conducted in retorts of glass or earthenware, either coated or uncoated.

6. ¶ By the action of sulphuric acid on bichromate of potassa.—3 parts of bichromate of potassa and 4 parts of ordinary sulphuric acid are heated together in a capacious retort; an evolution of oxygen gas, easy to regulate, is the result. $151{\cdot}5 KO, 2CrO^3$, and $196 HO, SO^3$ yield $287{\cdot}5$ $Cr^2O^3, 3SO^3 + KO, SO^3, - 36HO$, — and $24O$ (= 6·3 per cent. of the chromate). This process is more economical than the ignition of chlorate of potassa; for 2 parts of the bichromate yield as much oxygen as 1 part of the chlorate. The residue in the retort likewise possesses a certain value. (Balmain, *Pharmaceutical Journal*, 2, 92.) ¶

The third and fourth methods are the most economical; and, when the operations are well conducted, and the carbonic acid properly removed, the gas obtained by them is very pure. Oxygen gas may be collected either over water or over mercury.

* The most convenient and economical apparatus that can be used in this process, at least for moderate quantities of material, is a Florence flask fitted with a gas-delivery tube. Heat may be applied to it by means of a small iron pan filled with sand and placed over an argand lamp. [W.]

General Rules for the Collection and Preservation of Gases.

Since the vessel in which the gas is evolved always contains air, the gas must not be collected till there is reason to suppose that the air is wholly or nearly expelled. The gas is conducted from the generating vessel through a bent tube, the gas-delivery tube *c* (*App.* 34, 35, 37), and made to pass through a liquid. The gas-delivery tube is made of glass or lead, the latter material being very convenient on account of its flexibility: a glass tube may, however, be rendered flexible by joining two pieces together by means of a caoutchouc connecter. The gas is conducted into a liquid which will not absorb it rapidly, *e. g.* cold or warm water, solution of common salt, mercury, oil, &c., according to the nature of the gas. Over the aperture of the gas-delivery tube is adjusted a glass vessel—a bottle, for example—in an inverted position, so that the bubbles of gas as they issue from the end of the tube may rise into the vessel and displace the liquid. When a watery liquid is used, a portion of it, sufficient to occupy an inch or two of the neck of the bottle, is generally allowed to remain. The bottle is then closed with a cork, and removed from the liquid with its mouth downwards. This contrivance prevents any escape of the gas, which might otherwise take place if the temperature should rise and the elastic force of the gas be consequently increased. The cork likewise remains saturated with moisture, and prevents the ingress of air which might ensue if the elasticity of the gas were diminished by reduction of temperature. When gases are collected over mercury, glass stoppers smeared with grease may be used: these are likewise applicable when the gas is collected over water.

Oxygen and other gases not easily absorbed by water may likewise be collected in the *Gas-holder* (*App.* 38). This instrument consists of a hollow cylinder of sheet copper, divided by a partition *fg* into two unequal parts, the upper one, which is the smaller of the two, being open. A tube *ab* open at both ends, proceeds from the upper division nearly to the bottom of the lower. In the side of the lower division near the bottom there is a wide opening *e* which may be closed with a screw. A tube *cd* fitted with a stop-cock, serves to let the gas out of the vessel. When the gas-holder is to be used, the aperture *e* is closed, the tube *cd* opened, and the upper division filled with water. The water then flows through *ab* into the lower division and fills it up, while the air escapes through *cd*. When the lower division is completely filled with water, *cd* is closed, *e* opened, and the gas-delivery tube inserted into the opening. As the gas issues from the tube and collects in the upper part of the receiver, the water flows out by the aperture *e*. The height of the liquid is shown in the glass tube *h*, which communicates above and below with the lower division of the gas-holder. When the vessel is sufficiently full, the gas-delivery tube is withdrawn, the aperture *e* closed with the screw, and the upper division filled with water, to prevent the air from gaining access to the gas through the tube *ab*, in case of a fall of temperature occurring. To cause the gas to flow from the tube *cd*, it is only necessary to open the stop-cock with which that tube is furnished, and keep the upper division of the gas-holder filled with water. If it be desirable that the gas should issue under stronger pressure, a tube-funnel may be screwed into *a*, and kept full of water.*

* A much more convenient form of the gas-holder is that in which the upper and lower vessels are separate from one another, but connected by means of two tubes furnished with stop-cocks, one of the tubes just pass'ng through the top of the lower vessel, the

Properties of Oxygen. Colourless gas:—Specific gravity (Vol. I., p. 279).—Refractive power (Vol. I., p. 95).—Inflammable bodies burn in oxygen gas much more vividly than in common air; a glowing slip of wood introduced into it bursts into flame with a slight detonation. Nitric oxide gas mixed with it produces orange-red vapours. It is tasteless and inodorous. Animals enclosed in this gas would probably live longer than in an equal volume of confined air.

Combination of Oxygen with other Bodies.

Oxygen is capable of combining with all other known elements, with the single exception of fluorine, which is not so well known as the rest. Most substances, especially those of a decidedly electro-positive character, have greater affinity for oxygen than for any other substance, and evolve light and heat in combining with it. The combination of oxygen with other bodies, attended in this manner with evolution of light and heat, is called *Burning* or *Combustion*. In this process, the oxygen is the *Supporter of Combustion*,—the other body, the *Combustible* or *Burning Body*. Those substances which most resemble oxygen, viz., iodine, bromine, and chlorine (doubtless also fluorine)—and likewise nitrogen—show but little tendency to combine with it, and the combination is not attended with sensible evolution of heat: such bodies cannot therefore be classed among combustibles.

The combination of oxygen with other bodies does not always take place on mere contact: heat, light, electricity, compression, expansion, contact with platinum or certain other metals, or with another body already in process of oxidation—is often necessary to induce the combination to take place. (*See* Vol. I., pp. 35....38.)

But few bodies are capable of combining with oxygen *at ordinary temperatures;* and even those which exhibit this capacity lose it at temperatures still lower. The temperature required to induce the combination of any substance with oxygen—the *Burning Point*, as it may be called—is different, not only for different substances, but even for the same substance, according as the combustion is to take place rapidly or slowly. Thus, phosphorus combines slowly with oxygen, or exhibits *slow combustion*, at 25° (77° Fah.); but does not enter into *rapid combustion* till raised to 60° (140° Fah.) Charcoal likewise burns slowly below a red heat.

Light rarely brings about the combination of oxygen with combustible bodies: whether in so doing it exerts a specific action or merely acts by the heat which it produces, is a question not yet decided. (*See* Vol. I., pp. 164....166.)

Nitrogen cannot be made to unite with oxygen by elevation of temperature, excepting under peculiar circumstances; chlorine, bromine, and iodine, not at all by heat, only by substitution.

Most combustions induced by *Electricity* may be attributed to the heat evolved by the discharge: in the case of oxygen and nitrogen, however, this explanation will not suffice (I., 429).

Compression of the oxygen gas does not appear to facilitate combustion, unless it takes place rapidly, and is consequently attended with evolution of heat (I., 301). Thénard, however, found that wood does not take fire in oxygen gas under the ordinary pressure, at temperatures

other going nearly to the bottom. The apparatus and the mode of using it are too well known to need more particular description. (Vid. Graham, *Elements*, p. 245; Fownes' *Manual of Chemistry*, p. 96; Mitscherlich, *Lehrb.*, I, 6.)

below 350°; but under a pressure of 2·6^m, combustion begins at 252°.—On the other hand, phosphorus in oxygen gas or common air exhibits slow combustion at a temperature which is lower in proportion as the gas or air is more rarefied; and a mixture of oxygen and phosphuretted hydrogen, which under the ordinary atmospheric pressure requires a temperature of 116·7° to inflame it, does not take fire at 118° when the density is increased to 15 times its former amount; but if the mixture, contained in an inclined glass tube standing over mercury, be rarefied by setting the tube upright, combustion takes place at 20°.—Döbereiner likewise found (*J. pr. Chem.* 1, 114) that a mixture of equal measures of oxygen, hydrogen, and nitrogen gases contained in a detonating tube was always exploded by the electric spark, if the tube were open at the bottom, or merely closed with water; but not always, when the tube was closed by a cork,—the compression appearing to offer an obstacle to the continuation of the combustion.

Platinum and certain other Metals.—When a mixture of oxygen and a combustible gas is placed in contact with certain solid bodies, combination takes place between the oxygen and the stratum of the combustible gas immediately in contact with the surface of the body; even at low temperatures, in fact, a slow combustion takes place. By this, the temperature of the solid body is raised,—and consequently, the process of combustion is not only sustained but actually accelerated; and at length the temperature of the solid body may be so much raised as to give rise to rapid combustion. The larger the surface of the metal, the more powerful is its action.

It was observed by Sir H. Davy that a mixture of oxygen gas or common air on the one hand, and hydrogen, carbonic oxide, olefiant gas, cyanogen, or vapour of hydrocyanic acid, alcohol, ether, rock-oil, or oil of turpentine on the other, is brought into a state of slow combustion by contact with thin platinum foil or a spiral of platinum wire heated to a temperature short of redness,—that the heat thus developed brings the platinum to a state of bright ignition,—and that, with certain gases, rapid combustion at length ensues. He likewise found, as had been previously observed by Grotthuss, that the mixture of oxygen and hydrogen gases heated not quite to redness in a glass tube, passed in a few minutes into the state of combination and formed water, without sensible evolution of light and heat. Erman showed that the platinum wire requires a temperature of only 50° to 51° C. in order to induce the combination of oxygen and hydrogen. E. Davy found that his platinum-black (platinum in a state of division still finer than that of spongy platinum), moistened with alcohol, became incandescent in the air and induced combustion of the alcohol. Finally, Döbereiner discovered that freshly ignited spongy platinum (as it remains after ignition of ammonio-chloride of platinum) excites, even in the cold, first the slow, and then, under favourable circumstances, the rapid combustion of a mixture of hydrogen gas with oxygen or atmospheric air. It appears from the experiments of Döbereiner, Pleischl, and Dulong & Thénard, that this property is possessed (though in a less degree, so that in most cases the temperature must be raised, though never to the burning point), by other solid substances, both metallic and non-metallic, *e. g.* palladium, rhodium, iridium, osmium, gold, silver, cobalt, nickel, charcoal, pumice-stone, porcelain, glass, rock crystal, and fluor-spar.

These experiments may be made in either of the following ways:

1. Spongy platinum fastened to the end of a wire is suspended

within a glass flask, which is then exhausted of air and filled with the mixture of oxygen and the combustible gas.—2. The gaseous mixture is contained in a vessel standing over mercury, and the spongy platinum fastened to a wire is pushed up into it: or a piece of it is simply passed up by itself through the mercury into the gas. The platinum is best prepared for this purpose by forming a mixture of moistened clay and ammonio-chloride of platinum, or of sal-ammoniac and spongy platinum, into balls, and heating them gently: the balls thus prepared may be used several times.—3. The mixture of oxygen or air with the combustible gas is directed on the spongy platinum contained in a glass dish or a funnel.—4. The spongy platinum is attached to a fine platinum wire (for this purpose the platinum wire may be wound into a spiral, or a loose net may be made of it; and upon this a portion of ammonio-chloride of platinum made into a thick paste with a small quantity of water, may be fastened, and then ignited); a stream of the combustible gas is then to be directed upon it: the gas is thus brought in contact with the platinum after first mixing with the air.—5. Fine platinum wire is wound from three to eight times in a spiral form round a thin glass rod or an iron wire, the turns of the spiral being kept very close together: it is then removed, and inserted by its lower extremity into the end of a glass tube, from which the combustible gas issues into the air;—or the lower turns of the spiral are fixed round the wick of a lamp fed with a combustible and volatile liquid, such as alcohol, ether, or a volatile oil;—or again, the end of the wire is inserted into the middle of the wick or into a capillary tube into which the liquid rises. This arrangement (5) serves for the *Lamp without Flame* or *Glow-lamp*. It is usual to set fire to the vapour, and let it burn till the platinum wire becomes red hot;—then, when the flame is blown out, the wire continues to glow.—6. A triangle of fine platinum foil is cemented by one of its corners into a thin glass rod, which serves for a handle, and held (in some cases after being heated) over the aperture from which the combustible gas issues into the air,—or else over a volatile liquid, such as alcohol or ether.—The greater the purity of the ammonio-chloride, the more efficient is the spongy platinum prepared from it.—As with platinum, so also with the other metals above named.

Further particulars relating to this matter will be given in speaking of the different combustible gases, especially hydrogen.

The action of one burning substance on another will also be described under the head of *Hydrogen*.

That minute *Mechanical Division* renders many substances capable of burning at comparatively low temperatures, is shown by the following experiments. When oxide of nickel, cobalt, or iron is reduced by hydrogen gas at a temperature of about 360°, not quite amounting to redness, or when oxalate of iron is heated in close vessels not quite to redness, whereby the iron is reduced (according to Döbereiner, *Schw.* 62, 96, and Böttger, *Beiträge*, 2, 43, oxalate of protoxide of iron does not, when ignited, leave a residue of pure iron),—the metallic powder thus obtained burns with a glimmering light on being exposed to the air at ordinary temperatures. If the heat during the reduction be raised to redness, or if the metal reduced at a heat below redness be afterwards ignited in hydrogen gas, it will no longer exhibit spontaneous combustibility,—possibly, because the metal when thus strongly heated agglomerates in denser masses: but if a quantity of alumina or glucina be mixed with the metallic oxide,—by mixing the solution with that of

a salt of alumina or glucina and precipitating by an alkali—the metal, when reduced by hydrogen, even at a red heat (provided the heat has not been very intense), takes fire, on exposure to the air, as readily as that which has been reduced at a lower temperature; possibly, because the interposition of the earths, which are not reduced by the hydrogen, prevents the particles of metal from welding together. Copper reduced by hydrogen gas at a very moderate heat was likewise observed on one occasion to become covered, on exposure, with a film of oxide, without however taking fire. Iron reduced by hydrogen gas absorbs several times its volume of carbonic acid gas: it thereby loses its inflammability, which, however, it recovers by being again heated in hydrogen gas.—This property of spontaneous inflammability may be explained in two different ways: 1. The metal reduced by hydrogen retains a portion of this gas enclosed among its particles; and, when exposed to the air, it induces combination between this substance and the oxygen of the air (after the manner of Döbereiner's process); and the great heat evolved in this combination causes the metal to take fire. Against this, however, it may be alleged that iron reduced from the oxalate cannot contain hydrogen gas enclosed amongst its particles; and even when the metal is thrown into water, and the water driven off by evaporation, spontaneous combustion is still produced by contact of air.—2. The metal when exposed to the air absorbs the air mechanically, just as any porous body would do (and possibly it may absorb oxygen with peculiar avidity);—and the heat developed by this mechanical absorption gives rise to the combustion. If the metal has been previously saturated with carbonic acid gas, of which perhaps it absorbs a larger quantity than of oxygen, it does not become heated by contact with the air. (Magnus.)—Wöhler likewise found that intimate mixtures of charcoal and reduced metals often possess the property of taking fire at a red heat.

Development of Light and Heat in the Combination of Oxygen with other bodies.

Oxygen, in combining with electro-positive bodies, evolves a greater quantity of *heat* than any other substance. [For the different quantities of heat evolved by different substances during combustion, *vide* Vol. I., pp. 292....294.] The quantity of heat which one and the same combustible body evolves in combining with oxygen is undoubtedly the same, whether the combustion takes place slowly or quickly, provided only that the relative quantities of the combining bodies are the same in both cases. In the case of slow combustion, however, the heat is much less intense, and often becomes insensible; because, during the long time occupied in the combination, the greater part of it is carried away by conduction. It may perhaps be assumed that a body evolves more heat in combining with the first atom of oxygen than with the second, &c. &c.;—just as, according to the law stated on page 143, Vol. I., its affinity for oxygen is less as the quantity of that element already combined with it is greater. This, it must be observed, is contrary to Dulong's assertion, that one part of oxygen evolves 2688 units of heat in combining with carbon, and 3031 units in combining with carbonic oxide.—When oxygen previously combined with a body A is transferred to another body B, the heat evolved is less than that which would be developed by the combination of free oxygen with B; and the difference is probably equal to the quantity of heat previously evolved in the combination of the oxygen with A. The

quantity of heat evolved is greatest when the body A, with which the oxygen was previously combined, is either nitrogen, iodine, or chlorine; because, in its combination with these three substances, little or no heat appears to be evolved.

On the contrary, the quantity of *Light* evolved in the combination of oxygen with a given quantity of a combustible body varies greatly according to the rapidity of the combustion. If the combination takes place so slowly, that the heat evolved is not sufficiently intense to raise the surface of contact of the oxygen with the burning body to the point of incandescence or *glow-point*, then, generally speaking, no light is evolved. The only exceptions to this rule are the slow combustion of phosphorus and the phosphorescence of wood and various other organic bodies (Vol. I., pp. 181....192). On the contrary, the higher the temperature is raised above the glow-point by rapid combustion, the greater is the quantity of light emitted by a given quantity of the burning body. Coal gas gives the greatest quantity of light when the flame is made as large as it can be without occasioning deposition of carbon. An argand burner fed with 1¼ cubic feet of coal gas per hour gives as much light as one candle; with 2 cubic feet, as much as 4 candles; and with 3 cubic feet, as much as 10 candles: hence it appears that a double quantity of gas gives a tenfold quantity of light. (Graham, *Elements*, p. 426.)

The fire which accompanies the process of combustion appears either as *Glow* or *Incandescence**, when the burning body does not before combustion pass into the gaseous state,—or as *Flame*, when the burning body is previously converted into gas or vapour. In the former case, the heat evolved at the surface of contact of the oxygen gas and the solid or liquid body—charcoal or iron, for example—passes into that body and heats it to redness. The colour of the light emitted varies with the intensity of the heat. Feebly glowing coals emit a dull red light (*Cherry-red heat, dull* or *feeble glow*); when more strongly heated, they emit a yellowish red light (*Bright* or *full red heat*); at still higher temperatures, a yellow light (*Dull* or *commencing white heat*), then a yellowish white, then a greenish white, and lastly, a bluish white, intensely dazzling light (*Bright, full,* or *dazzling white heat; Incandescence*, properly so called).

When the combustible body is in the gaseous form—either originally, or in consequence of the heat required to cause it to burn—the heat is developed at the boundary between the oxygen and the combustible gas, accumulating both in the new compound and in the contiguous portions of uncombined oxygen and combustible gas; and the glowing of these elastic fluids exhibits itself in the form of *Flame*. The heat of flame often greatly exceeds the ordinary white heat; for, according to Sir H. Davy, a fine platinum wire held at the twentieth of an inch from an alcohol flame still appears incandescent. Flame consists of an inner, dark, and less heated space filled with the combustible gas, and of a glowing envelope which marks the boundary at which the combustible body and the oxygen come in contact and unite, with evolution of light and heat. (Symm.)—A piece of phosphorus placed on the wick of a spirit lamp will not burn till it is pushed outwards. If a piece of phosphorus be placed on a wooden support in the middle of a basin filled with alcohol, and the alcohol be set on

* This term *Incandescence* is commonly used in a general sense to denote luminosity produced by elevation of temperature. It would, however, be better to restrict the word to its proper etymological signification, viz., the state of *white-heat*. The shorter word *Glow*, identical with the German, *Glüh-en*, is much better adapted to express luminosity in the more extended sense. [W.]

fire, the phosphorus melts, but does not take fire till the alcohol is burnt away or extinguished, or till the flame is blown on one side, or air directed upon the phosphorus by means of the blowpipe. In a similar manner, a lighted candle will go out when placed in the midst of an alcohol flame. (Davies, *Ann. Phil.* 25, 447.)

The *Brightness* or *Illuminating Power of Flame* depends, not only on the degree of heat, but likewise on the presence or absence of solid particles which may act as radiate points. A flame containing no such particles emits but a feeble light, even if its temperature is the highest possible—the flame of hydrogen gas, for example. But in flames which do contain solid particles, the brightness increases with the temperature to which these particles are raised. Solid particles in a flame sometimes arise from the combination of the combustible body with oxygen, *e. g.* phosphoric acid or oxide of zinc in the combustion of phosphorus or zinc; sometimes, when the burning body is an organic hydro-carbon in the gaseous state, they consist of particles of carbon in the form of soot separated in the interior of the flame by the heat of the burning envelope. A dull flame becomes brighter by the introduction of a solid body in a finely divided state.

Supposing that light and heat consist of the same substance endued with different rates of motion, it would appear that this substance, to cause it to acquire the higher degree of velocity necessary to produce the effect of light, requires the presence of solid bodies which may act as Radiating Centres.

The following substances give a *Dull Flame:* hydrogen gas, carbonic oxide gas, sulphur, selenium, arsenic, alcohol—and likewise coal-gas when it is mixed with a sufficient quantity of air to cause it to burn without deposition of soot: phosphorus also burns with a dull flame in chlorine gas, because the chloride of phosphorus, which is the product of the combustion, remains in the gaseous state. (H. Davy.) When a spiral of platinum wire or a piece of asbestos is held in either of these flames, or some powdered oxide of zinc thrown into it, the solid matter immediately becomes white-hot, and emits a vivid light. (H. Davy.) Paper soaked in solution of chloride of calcium and burnt in the flame of a spirit lamp leaves a white network of ashes, which, when held in the feeblest alcohol flame, emits a brilliant light. (Talbot, *Phil. Mag. J.* 3, 114.)

Drummond's Light. Upon a ball of burnt chalk (quicklime), having a stem by which it is fastened to a wire, alcohol is projected from one set of tubes, while oxygen gas is blown upon it from another set. The alcohol burning in the oxygen gas heats the ball to the most dazzling whiteness; so that the light, when reflected by a concave mirror placed behind it, is plainly visible at the distance of 68 English miles. Zirconia gives a light somewhat less powerful than that of lime; that produced by magnesia is only half as strong. (Drummond, *Ed. J. of Sc.* 5, 319; also *Schw.* 48, 431; also *Pogg.* 9, 170.) By the oxy-hydrogen blowpipe (vid. *Hydrogen*) burnt chalk is rendered much more brightly luminous than by alcohol and oxygen gas. Supposing the intensity of light of a wax candle = 1, that emitted by a cylinder of lime whose circumference is one-fifth of that of the flame of the candle, is equal to 153 when it is ignited by the oxy-hydrogen flame; to 76, in the flame of ether and oxygen; to 69, in that of alcohol and oxygen; and to 19, in that of coal-gas and oxygen. Unburnt chalk, white clay, and magnesia, give much less light than burnt chalk. (Pfaff, *Pogg.* 40, 547.)—For experiments with

the flame of an oil lamp fed with oxygen, also with oil-gas and oil of turpentine, *vid.* Pleischl (*Zeitschr. Phys. Math.* 1, 390); Gaudin (*Compt. rend.* 6, 861; also *J. pr. Chem.* 16, 54).

Detonating gas, enclosed in a strong and perfectly dry glass globe, gives out a dazzling light when exploded, just like that of phosphorus burning in oxygen gas; if the density be doubled, the light is still brighter; but when the stop-cock is open, or the inner surface of the globe damp, the light is but feeble. (Döbereiner, *Schw.* 62, 87.) Probably the sides of the vessel become red-hot. (Gm.)

A *Bright Flame* is produced by the following bodies:—

1. Those which in combination with oxygen form a solid compound: phosphorus, potassium, antimony, bismuth, zinc, and most other metals. (Davy.)

2. Compounds containing carbon, from which a portion of the carbon is separated in the form of soot, by the heat produced at the part where the combustion actually takes place; the separated carbon being first brought to a state of vivid incandescence, and subsequently burnt when it comes in contact with oxygen. This is the case with marsh-gas, olefiant gas, ether, volatile oils, fats, resins, &c. (H. Davy.) The flame of alcohol may likewise be rendered bright by the presence of any substance which causes the carbon to separate from it. Thus, chlorine gas mixed with the flame of alcohol increases its luminosity, because, by combining with the hydrogen it causes a deposition of solid carbon. Vapour of binoxide of osmium likewise gives luminosity to the flame of alcohol, by giving up osmium and separating carbon from the alcohol. To produce this effect, a piece of osmium is laid on the edge of a piece of platinum-foil, and the foil held over the alcohol flame, so that the osmium may burn, and the vapours of the binoxide may mix with the vapour of alcohol (Berzelius). The more slowly a carbonaceous substance of this kind is burned, the greater is the quantity of carbon separated from it; the brightness of the flame is, however, diminished in the same proportion, because the particles of carbon are less strongly heated. On the contrary, the quicker the combustion, the smaller is the quantity of carbon separated; but the temperature to which it is raised is so much the higher, and consequently it emits a brighter light. (Payen, *J. Ch. Med.* 3, 177.)

The flame of these highly carbonized substances, *e. g.* that of a candle, consists of three parts: (*a*) The innermost part consists of gaseous matter produced by the decomposition of the tallow: this is at a temperature below redness. (*b*) The innermost cone is surrounded by a highly luminous envelope of finely divided carbon at a white heat. (*c*) This envelope is surrounded by a very pale blue flame, most plainly seen at the bottom. This pale flame marks the place where the combination of the oxygen supplied from without with the combustible matter evolved from the interior takes place; consequently this is by far the hottest part of the flame. (Symm. Porret, *Ann. Phil.* 8, 221; 9, 337; *compare* Longmire, *Ann. Phil.* 11, 176; Blackadder, *N. Ed. Phil. J.* 1, 52 and 224; Waldie, *Phil. Mag. J.* 13, 86; also *J. pr. Chem.* 15, 223.)

The *Size of the Flame* is *greater* in proportion as a greater quantity of oxygen gas is required to consume a given volume of the rising combustible gas, and also as the surrounding oxygen is mixed or combined to a greater extent with foreign gases; for in this case, the combustible gas must present a larger circumference and a greater number of points of contact to the oxygen, in order that the latter may be consumed as fast as it is supplied.

When different combustible gases are made to flow from a jet in streams of given strength into oxygen gas and mixtures containing it, the following effects are observed: Hydrogen gas gives a much smaller flame than olefiant gas (1 volume of hydrogen requires half a volume of oxygen, and 1 volume of olefiant gas requires 3 volumes of oxygen to burn it). Hydrogen gas mixed with nitrogen gives a still smaller flame than pure hydrogen. The flame of hydrogen gas in oxygen is smaller than that of the same gas in air; but there is this anomaly observed, that hydrogen gives a smaller flame in air than it does in chlorine or nitrous oxide gas,—although 1 volume of hydrogen gas requires 2·4 volumes of air and only one volume of chlorine or of nitrous oxide gas. This peculiarity is probably due to the different degrees of diffusibility of the gases through each other. (Waldie.)

The Colour of the Flame depends partly on its temperature, partly on the nature of the substances contained in it.

Cold carbonic oxide gas gives a blue flame in burning; but if it has previously been heated, it gives a yellowish red flame. Hydrogen and other gases which in burning evolve more heat than is evolved by carbonic oxide, exhibit a yellowish red flame even when set on fire in the cold. But when hydrogen gas issues from a fine jet (as in Marsh's apparatus) against a porcelain slab held close in front of it, a pale green flame is produced,—possibly in consequence of the cooling action of the porcelain. The blue flame at the lower part of the flame of a candle likewise indicates a comparatively low temperature. It is remarkable that in the glowing combustion of solid bodies the colours exhibit exactly the opposite relation (p. 28).

The addition of boracic acid, or of a metallic chloride and oil of vitriol to alcohol, gives the flame a green colour—or, when it is more strongly heated, turns it yellow. Chloride of strontium or chloride of calcium colours the flame of alcohol red; chloride of barium, or common salt, colours it yellow; proto-chloride of copper gives it a bright red colour, with green and blue edges. Copper covered with oxide or sulphide (but not clean copper) held in the flame of alcohol, colours it green. (Mulder, *N. Br. Arch.* 2, 145.) The flames of other burning bodies undergo similar alterations. Chloride of strontium reddens the flame of hydrogen, marsh-gas, and olefiant gas, as also that of a candle—but only so long as the salt itself remains moist; on the flame of sulphur it has no effect. (Hünefeld, *Schw.* 60, 383; *J. pr. Chem.* 7, 234.) In all these cases, a portion of the added substance undoubtedly volatilizes: but whether it volatilizes undecomposed, so that the colour of the flame is altered merely by the presence of boracic acid, chloride of strontium, chloride of copper, &c., or whether decomposition takes place, so that boron, strontium, calcium, barium, or copper is introduced into the flame in the reduced state—is there burnt—and thereby produces a different colour—is a question not yet decided. Sir H. Davy suggested the latter explanation.

In ordinary flames, the combustible gas occupies the interior, and is surrounded with atmospheric air or oxygen gas. But the combustion may likewise be sustained by directing a stream of oxygen gas, air, &c. into a vessel filled with the combustible gas. The interior dark part of the flame then consists of oxygen gas; and this gas seems, as it were, to burn in the combustible gas. In this manner, oxygen gas (and also chlorine) may be made to burn in hydrogen; likewise, oxygen gas,

common air, vapour of hyponitric acid (or chlorine gas, with large deposition of soot) in olefiant gas. To produce this effect, a stoppered bell-jar standing over water is filled with olefiant gas—the stopper removed—the gas set on fire—and the oxygen tube, which is fitted into a cork, plunged into the olefiant gas—the cork serving to close the aperture. Or a quantity of chlorate of potash contained in a small basin suspended from the cork may be heated till it evolves oxygen gas, and then plunged into the olefiant gas previously set on fire at the mouth of the jar: the combustion then goes on, producing a beautiful light, the colour of which may be variously modified by the addition of nitrate of soda, strontia, or copper (Kemp, *J. Pharm.* 20, 413; also *J. pr. Chem.* 3, 44).

The flame of oxygen in hydrogen gas is green, even when both gases are quite pure: that of oxygen in marsh-gas is yellow. The first-mentioned flame is much larger than the other, because a measure of oxygen gas requires two measures of hydrogen, and only half a measure of marsh gas (Hess, *Pogg.* 44, 336; also *J. pr. Chem.* 13, 516).

The flame is smaller when oxygen or nitrous oxide gas, or vapour of hyponitric acid (or chlorine gas) is made to pass into hydrogen gas, than in the contrary case: according to what was said on *page* 30, the contrary might have been expected. A much smaller flame is produced when oxygen passes into olefiant gas than when it passes into hydrogen. With olefiant gas, the flame is dark within,—then follows a brilliant envelope, hot enough to melt platinum,—then, towards the outside, a dark yellow flame, lengthening above and containing soot, the greater part of which remains unburnt. When oxygen gas is blown into boiling sulphur, a yellow flame is produced, dark within, red on the outside and at the apex: air gives a smaller flame than oxygen, dark within, blue without, and red at the apex (Waldie, *Phil. Mag. J.* 13, 86).

The *Blow-pipe Flame* must also be mentioned in this place, inasmuch as the air is blown into the middle of the ascending combustible vapour. The strongest heat exists at that part of the flame where the dark cone of injected air terminates in a bluish vertex, and the burning envelope which surrounds it concentrates itself upon a single point.

When the slow or rapid combination of a body with oxygen has once been set up by elevation of temperature, the continuance of this combination, after the supply of heat from without has been withdrawn, depends in general on the following condition;—whether the quantity of heat which the body in combining with oxygen evolves in a given time, is equal to that which, in the same time, is carried away by surrounding bodies; and consequently, whether the body remains at the temperature necessary for combustion;—and in particular: 1. On the difference between the temperature at which the body will combine with oxygen, rapidly or slowly, and the external temperature; 2. On the quantity of heat which it evolves in burning; 3. On the rarefaction or condensation of the oxygen gas; 4. On the greater or smaller admixture of foreign gaseous bodies not contributing towards the combustion; 5. On the presence of liquid or solid heat-conducting bodies.

1′*. Iron and diamond require a white heat to make them burn rapidly: hence, when heated in the air till they begin to burn, the combustion ceases as soon as the access of heat from without is discontinued; whereas sulphur and other easily inflammable bodies continue to burn.

* The accented numbers at the head of this and the four following paragraphs refer to the numbers in the preceding paragraph.

2'. Carbonic oxide gas, which is as easily inflammable as hydrogen, does not exhibit rapid combustion after it has been rarefied to about one-fourth of its ordinary density, because it evolves less heat during combustion. (H. Davy, *vide* p. 292, Vol. I.)

3'. A certain degree of rarefaction prevents the continuance of combustion; because combination, and therefore, also, development of heat, is retarded by it. Detonating gas, (a mixture of two measures of hydrogen gas and one of oxygen,) when rarefied to $\frac{1}{18}$ of its ordinary density, no longer explodes by the electric spark. (H. Davy.) Hydrogen gas, mixed with air in the right proportion, will not take fire under an external pressure of 5 inches. (Grotthuss.) Hydrogen gas issuing from a jet into the air exhibits rapid combustion under a fourfold rarefaction of the air, burning even with a larger flame than before, but is extinguished when the density is reduced to between $\frac{1}{7}$ and $\frac{1}{8}$ of its ordinary amount.

The burning vapour of alcohol, ether, or wax, is extinguished, under these circumstances, by a five or sixfold rarefaction, sulphuretted hydrogen by a sevenfold rarefaction of the air. Sulphur continues to exhibit rapid combustion, even when the air is rarefied 15 times; phosphorus, when the density is reduced to $\frac{1}{60}$; while the easily inflammable variety of phosphuretted hydrogen gas produces a flashing light, even in the best vacuum that can be made with the air-pump. Vapour of ether in air rarefied 30 times, still produces a feeble flame on the introduction of a red-hot iron. Slow combustion on the surface of platinum is exhibited by marsh-gas, down to a fourfold rarefaction of the air; by carbonic oxide, to sixfold; by vapour of alcohol, ether, or wax, to eightfold; by olefiant gas, to ten or elevenfold; by hydrogen gas, to thirteenfold; and by vapour of sulphur, down to twentyfold rarefaction of the air. By elevation of temperature, the limits of inflammability are still further extended; so that detonating gas rarefied 18 times and heated to redness, exhibits a light, as if from combustion, on the passage of an electric spark. (H. Davy.) According to Grotthuss, on the contrary, inflammability is diminished by heating, provided the heat can produce expansion; so that, for example, a mixture of hydrogen gas and air expanded in the Torricellian vacuum, to such a degree only that it would be inflammable by the electric spark at ordinary temperatures, loses its inflammability when still further expanded by heat. Grotthuss therefore concludes that when expansion can take place freely, heat possesses the power (1) of expanding the body and thereby diminishing its inflammability; (2) of inducing it to take fire. He also infers that the expansion takes place according to an arithmetical, the increase of inflammability according to a geometrical progression; and that, consequently, at a certain degree of heat, which, however, when the gaseous mixture has been previously expanded in the Torricellian vacuum, must be very considerable, the latter must gain the victory. Davy, on the contrary, found that detonating gas standing over mercury, and gradually heated till it was expanded to $2\frac{1}{2}$ times its original volume, was inflamed as the temperature ultimately reached a red heat: he supposes that in Grotthuss' experiment the combustion was prevented by the presence of aqueous or mercurial vapour.

4'. Foreign gaseous bodies, which contribute nothing to combustion, absorb a portion of the heat generated by the combination, and reduce the temperature below the burning point, the rapidity of their action

being proportional to their quantity, mobility, and capacity for heat. Not only do bodies in general burn more rapidly in oxygen gas than in atmospheric air, which contains only one volume of oxygen to four of nitrogen; but iron and diamond, which, when once set on fire, continue to burn in oxygen gas, are immediately extinguished in atmospheric air. In air four or five times compressed—which, therefore, contains one volume of oxygen gas—candles, hydrogen gas, sulphur, charcoal, and iron, do not, in consequence of the abstraction of heat by the nitrogen, burn more rapidly than they would in uncompressed air, to which $\frac{1}{4}$ of a volume of oxygen had been added. One volume of detonating gas loses its power of taking fire by the electric spark, if there be added to it $\frac{1}{2}$ a volume of olefiant gas, $\frac{4}{5}$ of a volume of fluoride of silicium, 1 volume of marsh-gas, 2 volumes of hydrosulphuric or hydrochloric acid gas, 8 volumes of hydrogen in excess, 9 volumes of oxygen in excess, or 11 volumes of nitrous oxide: 5 measures of aqueous vapour do not destroy the inflammability of 1 measure of detonating gas. (H. Davy.) According to Humboldt and Gay-Lussac (*Gilb.* 20, 49), the inflammability of one volume of detonating gas is destroyed by the admixture of 5 volumes of oxygen, or 4·7 volumes of hydrogen gas. Marsh-gas is no longer inflammable by the electric spark, when it is mixed with 11 measures of oxygen instead of the 2 measures which it actually requires to combine with it. (H. Davy.) Coal gas burns continuously in a mixture of 1 measure of oxygen and 7 of nitrogen, but is extinguished when the quantity of the latter amounts to 8 measures; it burns in a mixture of 1 measure of oxygen, with 3, but not with 4 measures of hydrochloric acid gas; with $2\frac{1}{2}$, but not with 3 measures of carbonic acid; with 2, but not with $2\frac{1}{2}$ measures of fluoride of silicium. The greater the density of the inactive gas, the smaller is the quantity which suffices to stop the combustion; because the combustible gas diffuses itself more readily through a heavy than through a light gas, and therefore cools down the faster. (Waldie.) A lighted candle is extinguished in air to which $\frac{1}{4}$ of its volume of hydrochloric acid gas, or $\frac{1}{10}$ of fluoride of silicium has been added. When combustible bodies burn in a confined space, the relative quantity of nitrogen, &c. becomes increased, partly by consumption of oxygen, partly by formation of gaseous products of combustion, such as carbonic acid, sulphurous acid, &c.; and thus the combustion is brought to an end. In one and the same limited space, a candle goes out first, then hydrogen gas, then sulphur; while the slow combustion of phosphorus will go on as long as the smallest quantity of oxygen remains. (H. Davy.)

5'. Solid burning bodies are extinguished when laid on good-conducting supports, *e. g.* glowing coals on considerable masses of metal.—A mixture of combustible gases and oxygen will not take fire in very narrow tubes, because their sides cool down too quickly (this is the principle of Newman's oxy-hydrogen blow-pipe). From the same cause, the flame of a mixture of combustible gases and common air is often unable to pass through the meshes of wire-gauze: the passage of the flame takes place, however, with greater facility, the lower the temperature at which the gas takes fire, the greater the heat evolved by its combustion, the more quickly it is forced through the apertures by pressure or draught, the wider the meshes, the smaller the mass and specific heat of the metal of which the gauze is made, and the higher its temperature. Above a certain temperature, all flames pass through it.—On this impenetrability of wire-gauze by the flame of light carburetted

hydrogen gas occurring in coal-mines, is based the *Safety-lamp* of Sir H. Davy (*Ann. Phil.* 25, 154).—The flame of a cotton thread may be extinguished by holding over it, even at some distance, a ring of fine iron wire or a thicker ring of glass. (H. Davy.)

According to McKeever (*Ann. Phil.* 26, 344; also *Schw.* 48, 42), a wax or tallow candle burns out more quickly in the dark than in sunshine, although under the latter circumstances the temperature is much higher.

Motion of the air produced by draught or by the bellows accelerates combustion, and thereby increases the intensity of the heat,—inasmuch as it continually brings fresh portions of air in contact with the burning body.

Wind-furnace; Blast-furnace. Sefström's blast-furnace (*Pogg.* 15, 612), altered by Mohr for operations on the small scale (*Ann. Pharm.* 27, 229), is peculiarly well adapted for chemical purposes.

For burning any substance in a confined space with continual renewal of air, and collecting the product of the combustion, Brunner's *Aspirator* (*Pogg.* 38, 264)—an apparatus which is applicable to a variety of purposes—may be conveniently employed. It consists generally of a vessel filled with water. The water is let out at the bottom; and as it escapes, air enters at the upper part, having been previously made to pass over the substance which is to be submitted to its action (*App.* 39). When all the water has run out, the vessel must be refilled by the middle tube. Modifications of the apparatus have been made by Abendroth (*Pogg.* 53, 617), and Bolley (*Ann. Pharm.* 41, 322).

Very rapid motion of the air may extinguish a burning body,—either by cooling, if the quantity of air supplied in a given time is such that the burning body cannot in that time consume the whole of its oxygen; *e. g.* in the case of red-hot coke; or by blowing the burning vapour away from its source, so that the flame can no longer communicate with the fresh matter which issues: *e. g.* the extinction of a taper.

Fire-extinguishing substances act either by cooling, as water does,—or by covering the burning body, and thereby impeding the access of air: *e. g.* saline solutions, loam-water, &c.

By the most exact experiments, first instituted by Lavoisier, it has been established, that in combustion the whole of the ponderable matter in the oxygen gas combines with the whole of the ponderable matter in the burning body; so that the new substance produced by the combustion—the burnt body—weighs exactly as much as the oxygen gas consumed and the combustible body consumed taken together. This is the *Antiphlogistic Theory of Combustion.*

The establishment of this theory overthrew the *Phlogistic Doctrine* of Stahl and others, according to which it was assumed that every combustible body is composed of *Phlogiston*—a peculiar, imponderable principle of combustibility, common to all bodies—and an acid or earthy substance (*e. g.* phosphorus, of phlogiston and phosphoric acid; lead of phlogiston and lead-earth or calx of lead, the substance now called oxide of lead); that, when combustion takes place, the phlogiston escapes and the substance with which it was combined remains in the form of the earthy matter; that, on heating the burnt body in contact with charcoal, a body very rich in phlogiston, the burnt body again takes phlogiston from the charcoal and is restored to the state of a combustible

body. In short, wherever the present theory asserts that a body takes up oxygen, the former theory assumed that it parts with phlogiston; and wherever, according to the present view, oxygen is taken from a body, it was supposed, according to the former view, that phlogiston is added to it. If the phlogistic doctrine were true, the body which remains after combustion ought to weigh less than the combustible body—which is contrary to fact.*

It now only remains to investigate the cause of the development of light and heat in combustion.

1. Lavoisier attributed it to the latent heat which imparts the gaseous form to the ponderable part of oxygen gas—the oxygen, properly so called—and is separated during the combination of the oxygen with other bodies. That this assumption is inadmissible, is evident from what was said on page 297, b, Vol. I.

2. It is supposed that simple substances contain, independently of the heat of fluidity which may belong to them, another and larger quantity of heat still more intimately combined; and that this latter quantity is set free when they enter into combination with ponderable bodies. This view of the matter resolves itself into three others.

a. The oxygen alone contains heat thus intimately combined, and gives it up on combining with combustible bodies. Brugnatelli makes a distinction between *oxygen* properly so called—the ponderable body in fact—and *therm-oxygen*, or oxygen containing intimately combined heat or fire. Oxygen gas he supposes to be therm-oxygen combined with heat of fluidity, which gives it the gaseous form. In nitre, chlorate of potash, &c., the the therm-oxygen is supposed to have parted with its heat of fluidity, but to have retained this more intimately combined heat; but when oxygen is transferred from these compounds to carbon, phosphorus, sulphur, metals, &c., the intimately combined heat is set free, and consequently the compounds formed by the combustion of these substances contain merely the oxygen, separated from all the heat with which it was associated. In support of this theory, we might adduce the observation of Welter (I. 294), viz. that a pound of oxygen evolves the same quantity of heat whether it combines with the equivalent quantity of hydrogen or of carbon. Since, however, in the combination of oxygen with other combustible bodies, different quantities of heat are evolved, Brugnatelli's theory cannot be true,—excepting on the supposition that, in the combination of oxygen with various combustible bodies, the heat which belongs to it (independently of the heat of fluidity) is sometimes more, sometimes less completely set at liberty; and consequently, a quantity of it, variable according to the nature of the combustible body, remains behind in the new compound.

b. The intimately combined heat exists only in the combustible body,

* The advocates of the phlogistic theory endeavoured to get over this difficulty by ascribing to phlogiston a principle of absolute *Levity*. Now, however improbable such a supposition may be, it by no means involves an absurdity: for this supposed *principle of levity* would simply amount to a tendency to *recede* from the earth, instead of approaching it as ponderable bodies do; and no one can say that the existence of a body having such a tendency is an impossibility. The real superiority of the antiphlogistic theory consists in this: that it ascribes the observed increase of weight to the addition of a real, tangible substance, which can actually be separated, collected, and weighed; whereas, the phlogistic theory was obliged to rest its conclusions on the existence of a substance purely hypothetical. [W.]

and is set free when that body combines with oxygen. This was the idea of Wiegler, who thereby, to a certain extent, endeavoured to rescue the notion of phlogiston, by supposing it to be the same as intimately combined heat.

c. The intimately combined heat exists in all elementary bodies, both combustibles and supporters of combustion. In the act of combustion, both the heat thus combined with the oxygen and that combined with the combustible body is set free. This theory has much probability in its favour.

3. *Electro-chemical Theory of Combustion.* Oxygen contains one kind of electricity in a state of combination; the combustible body, the other kind. In the act of combustion, the two electricities unite and form heat. Views of this kind were first enunciated by Wilkie (*Crell. Ann.* 1788, 1, 414), afterwards by Grotthuss (*Ann. Chim.* 63, 34).

a. Oxygen contains negative electricity in combination; the combustible body, positive electricity. (Berzelius.)

b. Oxygen contains positive, the combustible body, negative electricity. This is the hypothesis adopted in the present work (I., 157, 342, 431); it does not, however, preclude the idea of the simultaneous liberation of heat or caloric previously existing in the body in a state of intimate combination, as described in 2, *c.*

The following less tenable theories of combustion, some phlogistic, others antiphlogistic, have also been advanced.

1. Gren and Wiegler: The combustible body consists of the substance which remains behind after combustion, and another substance, Phlogiston, possessing actual levity. When the body burns, this phlogiston escapes, and combines with the oxygen gas or dephlogisticated air, producing nitrogen gas or phlogisticated air, less both in weight and volume than the oxygen. In the combustion of bodies in *pure* oxygen gas, no nitrogen remains behind.

2. Kirwan: Combustible bodies consist of a *substratum* and phlogiston, which latter is identical with inflammable air (hydrogen gas). In the act of combustion, the phlogiston combines with the oxygen gas, from which it drives out the fire, and forms carbonic acid,—or, at higher temperatures, water. These products are sometimes set free; sometimes they combine with the substratum, and thus produce the various kinds of burnt bodies. This theory is directly contradicted by facts.

3. Van Mons: Combustible bodies consist of a substratum and hydrogen. In combustion, the hydrogen combines with the oxygen, forming water; and the water, uniting with the substratum, produces the burnt body: so that the combustible is substratum + hydrogen; the burnt body, substratum + water, or combustible + oxygen.

4. Scheele: The phlogiston of combustible bodies has but little weight. Oxygen gas or fire-gas consists of a saline matter having but little weight, together with water and a small quantity of phlogiston. In the act of combustion, the phlogiston of the combustible body combines in various proportions with the saline matter of the fire-gas, producing light and heat; and the water of the fire-gas is transferred to the substratum of the combustible body. But the burnt body weighs exactly as much as the combustible body consumed and the oxygen taken together.

5. Richter: The imponderable phlogiston of combustible bodies enters into combination with the heat of fluidity of the oxygen gas, and produces light, while the ponderable part of the oxygen combines with the ponderable part of the combustible body.

6. Göttling: Phlogiston is identical with light: and it partly combines with the *principle of fire* contained in oxygen gas (I., 167), and forms heat.

Compounds of Oxygen.

The act of combination of oxygen with other bodies is called *Oxygenation* (*Combustion*); also *Acidification*, when the resulting compound is of an acid nature; *Oxidation*, in the contrary case. The oxygen is the *Oxygenising* body (*Supporter of Combustion*); also according to circumstances—the *Acidifying* or the *Oxidizing* body. The body which combines with it is the *Oxygenizable* (*combustible*) body; also the *Acidifiable* or *Oxidable* body, as the case may be. The new compound is the *Oxygenized* (*burnt*) body; the *Acidified* body in the one case, the *Oxidized* or *Oxidated* body in the other. The separation of oxygen from another body is called *Deoxygenation*, *Deacidification*, *Deoxidation*, *Reduction*, or *Restoration*.

The combination of oxygen with other bodies takes place according to the following atomic proportions:

2 : 1	1 : 1	1 : 2	1 : 3	1 : 4	1 : 5	1 : 7
Ca^2O	HO	CO^2	CrO^3	NO^4	PO^5	ClO^7
	2 : 3	2 : 5	3 : 4	3 : 5	4 : 5	
	Fe^2O^3	S^2O^5	Mn^3O^4	S^3O^5	S^4O^5	

Most substances are capable of uniting with oxygen in more than one proportion; they have several *Degrees of Oxidation*.

Oxygen forms about 136 inorganic compounds: they are as follows:

1. Of acid nature: *Oxygen-acids*, *Oxacids*. These bodies exhibit the properties of acids (p. 3) in very different degrees. When the same radical forms several acids with different quantities of oxygen, that which contains the largest quantity of oxygen is invariably the strongest acid. Acids are named by affixing the terminations *ic* and *ous** to the name of the radical, sometimes immediately, sometimes after removing the last syllable. When a body forms but one acid with oxygen, the name of that acid ends in *ic*: thus carbon forms *carbon-ic* acid: when two acids are formed, the one which contains the larger quantity of oxygen is distinguished by the termination *ic*, the other by the termination *ous*: *e. g.* SbO^3 = antimonious acid; SbO^5 = antimonic acid. When more than two acids are formed, the two most important are designated in the manner just described: *e. g.* SO^2 = sulphurous acid, SO^3 = sulphuric acid; and the others are further distinguished by the prefixes *Hypo* for the lower degrees of oxidation, *Hyper* for the higher: examples will be seen in the following paragraphs. The combination of oxygen-acids with salifiable bases produces the *Oxygen-salts* or *Oxisalts* (p. 5).

The Oxygen-acids are divided into:

a. *Non-metallic Oxygen-acids*: Carbonic acid, CO^2;—boracic acid, BO^3;—hypophosphorous acid, PO,—phosphorous acid, PO^3,—phosphoric acid

* This and the following paragraphs relating to the nomenclature of oxygen-compounds are not translations of the corresponding paragraphs in the original, but contain an explanation of the English nomenclature given in the same order as that in which the author describes the German nomenclature. [W.]

PO^5;—hyposulphurous acid, SO,—sulphurous acid, SO^2,—sulphuric acid, SO^3,—pentathionic acid, S^5O^5,—tetrathionic acid, S^4O^5,—trithionic acid, S^3O^5,—hyposulphuric acid, S^2O^5;—selenious acid, SeO^2,—selenic acid, SeO^3; iodic acid, IO^5,—periodic or hyperiodic acid, IO^7;—bromic acid, BrO^5; —hypochlorous acid, ClO,—chlorous acid, ClO^4,—chloric acid, ClO^5, —perchloric or hyperchloric acid, ClO^7;—nitrous acid, NO^3,—hyponitric acid, NO^4,—nitric acid, NO^5.

b. *Metallic Oxygen-acids:* (Silicic acid, SiO^2);*—(titanic acid; TiO^2);—tantalous acid, TaO^2,—tantalic acid TaO^3; niobic acid, NbO^2(?); —pelopic acid, PeO^2(?);—tungstic acid, WO^3;—molybdic acid, MoO^3;—vanadic acid, VO^3;—chromic acid CrO^3;—manganic acid MnO^3,—permanganic or hypermanganic acid, Mn^2O^7;—arsenious acid, AsO^3;—arsenic acid, AsO^5;—antimonious acid, SbO^3,—antimonic acid, SbO^5;—(tellurous acid, TeO^2),—telluric acid, TeO^3;—(stannic acid, SnO^2);—ferric acid, FeO^3;—cobaltic acid, CoO^2(?);—ruthenic acid, RuO^4;—and osmic acid, OsO^4.

2. Compounds not of acid nature: *Oxides.* When a metal, by combining with different quantities of oxygen, forms two oxides belonging to the same class, these compounds are sometimes distinguished in the same way as acids, viz. by adjectives ending in *ous* and *ic*: but more frequently they are named according to the relative numbers of atoms of metal and oxygen which they contain: thus, one atom of metal with one atom of oxygen forms a *Protoxide;* 1 At. metal with 2 At. oxygen, a *Bi-oxide, Binoxide* or *Deutoxide;* 1 At. metal with 3 At. oxygen, a *Teroxide;* 1 At. metal with 4 at. oxygen; a *Quadroxide;* 2 At. metal with 3 At. oxygen, a *Sesqui-oxide;* 2 At. metal with 1 At. oxygen, a *Di-oxide* or *Dinoxide.*

Oxides may be divided into three classes, as follows:—

a. *Salifiable Oxides:* Oxides having the character of salifiable bases. These are:

α. Alkalis (p. 4). Potassa *or* potash, KO;—soda, NaO;—lithia, LO;—baryta, BaO;—strontia, SrO;—lime, CaO;—oxide of ammonium, NH^4O, may also be placed in this group.

β. Earths (p. 4). Magnesia, MgO;—lanthana *or* protoxide of lanthanum, LaO;—oxide of didymium, DiO(?);—protoxide of cerium *or* cerous oxide, CeO,—sesquioxide of cerium *or* ceric oxide, Ce^2O^3;—yttria, YO;—glucina, GO;—alumina, Al^2O^3;—thorina, ThO;—zirconia, ZrO;—(silica, SiO^2).

γ. Basic Heavy Metallic Oxides: Protoxide of titanium *or* titanous oxide, TeO (?),—(bi-oxide of titanium *or* titanic oxide, TiO^2);—protoxide of molybdenum *or* molybdous oxide, MoO,—bi-oxide of molybdenum *or* molybdic oxide, MoO^2;—bi-oxide of vanadium *or* vanadic oxide, VO^2;—protoxide of chromium *or* chromous oxide, CrO,—sesqui-oxide of chromium *or* chromic oxide, Cr^2O^3;—protoxide of uranium *or* uranous oxide, UO;—sesqui-oxide of uranium *or* uranic oxide, U^2O^3; —protoxide of manganese *or* manganous oxide, MnO,—sesqui-oxide of manganese *or* manganic oxide, Mn^2O^3;—ter-oxide of antimony *or* antimonic oxide, SbO^3;—(bi-oxide of tellurium *or* telluric oxide, TeO^2); —sesqui-oxide of bismuth, Bi^2O^3;—oxide of zinc, ZnO;—oxide of cadmium, CdO;—protoxide of tin *or* stannous oxide, SnO,—(bi-oxide of tin *or* stannic oxide, SnO^2);—protoxide of lead *or* plumbic oxide, PbO;—protoxide of

* Acids and bases whose names are enclosed within brackets are *amphoteric bodies*, that is to say, they have a very weak acid, and likewise a very feeble basic character, and will, therefore, be again mentioned among the salifiable bases.

iron *or* ferrous oxide, FeO,—sesqui-oxide of iron *or* ferric oxide, Fe^2O^3;—protoxide of cobalt *or* cobaltous oxide, CoO,—sesqui-oxide of cobalt *or* cobaltic oxide, Co^2O^3;—protoxide of nickel, NiO;—di-oxide of copper *or* cuprous oxide, Cu^2O,—protoxide of copper *or* cupric oxide, CuO;—di-oxide of mercury *or* mercurious oxide, Hg^2O,—protoxide of mercury *or* mercuric oxide, HgO;—di-oxide of silver *or* argentous oxide, Ag^2O, (?),—protoxide of silver *or* argentic oxide, AgO;—ter-oxide of gold *or* auric oxide, AuO^3;—protoxide of platinum *or* platinous oxide, PtO,—bi-oxide of platinum *or* platinic oxide, PtO^2;—protoxide of palladium *or* palladious oxide, PdO,—bi-oxide of palladium *or* palladic oxide, PdO^2;—protoxide of rhodium *or* rhodious oxide, RO,—sesqui-oxide of rhodium *or* rhodic oxide, R^2O^3;—protoxide of iridium *or* iridious oxide, IrO,—sesqui-oxide of iridium, Ir^2O^3,—bi-oxide of iridium *or* iridic oxide, IrO^2,—ter-oxide of iridium, IrO^3;—protoxide of ruthenium *or* ruthenious oxide, RuO,—sesqui-oxide of ruthenium, Ru^2O^3,—bi-oxide of ruthenium *or* ruthenic oxide, RuO^2;—protoxide of osmium *or* osmious oxide, OsO,—sesqui-oxide of osmium, Os^2O^3,—bi-oxide of osmium *or* osmic oxide, OsO^2,—ter-oxide of osmium, OsO^3.

b. Oxides which are either wholly incapable of combining with other bodies, or form a few very unstable compounds, and possess neither acid nor basic properties, because they contain too little oxygen: by taking up more oxygen, they are converted either into acids or bases.—*Suboxides.*

a. Non-metallic Suboxides: These, by taking up more oxygen, are converted into acids: carbonic oxide, CO;—oxide of phosphorus *or* phosphoric oxide, P^2O;—oxide of selenium *or* selenic oxide, SeO (?);—protoxide of nitrogen *or* nitrous oxide, NO;—bi-oxide of nitrogen *or* nitric oxide, NO^2.

β. Metallic Suboxides.—These, by addition of oxygen, are rarely converted into acids, more frequently into bases. Those with a note of interrogation after them are doubtful, probably mere mixtures of metal with a higher oxide: suboxide of potassium (?),—suboxide of sodium (?);—tungstous suboxide, WO^2,—tungstic suboxide, W^2O^3;—suboxide of vanadium, VO;—suboxide of arsenic;—suboxide of antimony (?);—suboxide of bismuth (?);—aurous suboxide, AuO,—auric suboxide.

c. Oxides which form scarcely any compounds, because they contain too much oxygen to form bases, and too little to form acids. By taking up a larger quantity of oxygen, some of them are converted into acids. *Peroxides* or *Hyperoxides.**

a. Non-metallic Peroxide: Peroxide of hydrogen, (sometimes also deroxide of nitrogen, NO^4).

β. Metallic Peroxides: Peroxide of potassium;—of sodium;—of lithium;—of barium, BaO^2;—of strontium;—of calcium;—of manganese, MnO^2;—of bismuth;—plumbous peroxide (red lead), Pb^3O^4,—plumbic peroxide, PbO^2;—peroxide of nickel, Ni^2O^3;—peroxide of silver.

d. Water stands apart from all these oxides. In some of its compounds, it plays the part of an acid; in others, that of a base: but it cannot be said to belong to either class in particular.

* The term *Peroxide* is often used in English nomenclature to denote merely the highest degree of oxidation of a metal, irrespective of basic or non-basic properties; but it would be as well if this use of it were abandoned. [W.]

CHAPTER II.

HYDROGEN.

Composition of Water.

Scheele. *Crell. Ann.* 1785, 2, 229, and 291.
Cavendish. *Crell. Ann.* 1785, 1, 324.
Watt. *Crell. Ann.* 1788, 1, 23, and 136.
Meusnier & Lavoisier. *Crell. Ann.* 1788, 1, 354, 441, and 528.
Lavoisier. *System der-antiphlogistischen Chemie;* übers. *von Hermbst.* S. 123.
——— Apparent conversion of Water into Earth. *Crell. Chem. J.* 3, 151.
Berzelius & Dulong. *Ann. Chim. Phys.* 15, 386.
Dumas. *Comptes rendus.* 14, 537.

Oxy-hydrogen Blowpipe.

Hare. *Ann. Chim.* 45, 113; abstr. *Gilb.* 55, 43
Phil. Mag. 50, 106; also *Scher. Ann.* 3, 250.
Brooke. *Ann. Phil.* 7, 367.
Newman. *Quart. J. of Sc.* 1, 65; 2, 379; also *Schw.* 18, 225, and 333; also *Gilb.* 55, 1. and 7.
Clarke. *Quart. J. of Sc.* 2, 104; also *Schw.* 18, 228.—*Ann. Phil.* 8, 313, and 357; 9, 89, 162, 194, and 326; 10, 133, and 373; 17, 419; partly also in *Schw.* 21, 382; also *Gilb.* 62, 247, and 339; also *Scher. Ann.* 3, 221.
Faraday. *Quart. J. of Sc.* 2, 461; also *Schw.* 18, 337.
Lampadius. *Schw.* 19, 319.
Ridolfi. *Schw.* 20, 218.
Pfaff. *Schw.* 22, 385.
Gay-Lussac. *Ann. Chim. Phys.* 14, 302.
Chodkiewicz. *Scher. Ann.* 3, 248.
Cooper. *Scher. Ann.* 5, 245.
Hübenthal. *Scher. Ann.* 244.
Parrot. *Scher. Ann.* 3, 239; 7, 280.—*Pander Beitr. zur Naturgesch.* 1, 50.
Skidmore. *Sill. Am. J.* 5, 347; also *Schw.* 39, 359.
Holme, Edwards, Beale, Clarke, Gray, Booth, Osbrey, Barchard, and others. *Ann. Phil.* 8, 470; 9, 167, 252, 253, 402, 481, and 483; 10, 66, 67, and 366; abstr. *Gilb.* 62, 270.—Watt. *Ann. Phil.* 11, 386.—Leeson. *Ann. Phil.* 14, 234.
Schmidt. *Gilb.* 66, 84.
Herrmann & Bischof. *Schw.* 56, 123.
Rutter. *Phil. Mag. J.* 1, 470.
Hemming. *Phil. Mag. J.* 1, 32.
Bischof. *J. pr. Chem.* 14, 129.
Daniell. *Phil. Mag. J.* 2, 57; abstr. *Pogg.* 25, 635.

Excitement of Combustion by Platinum,—see the papers cited on page 19.

Water of Hydration and Crystallization.

Berzelius. *Gilb.* 40, 246.
Graham. *Phil. Mag. J.* 6, 327; also *Pogg.* 38, 123; also *J. pr. Chem.* 5, 90.—*Ann. Pharm.* 29, 1.—*Elements*, 169.
Fremy. *J. Pharm.* 11, 169; abstr. *Ann. Pharm.* 64, 223; also *Q. Journ. Chem. Soc.* 1, 380.

Absorption of Gases by Water.

Priestley. *Americ. Trans.* 5, 21; *Crell. Ann.* 1798, 1, 40; and in *Exp. and Obs. on Air.* 2, 263.—Cavendish. *Phil. Trans.* 56, 161.—Berger. *J. Phys.* 57, 5; also *Gilb.* 20, 168. Dalton. *Manchester Memoirs, Sec. Ser.* 1, 284; 5, 11; *N. Syst.* 1, 219; *Ann. Phil.* 7, 215; also *Schw.* 17, 160.—W. Henry. *Phil. Trans.* 93, 29, and 274; partly also in *Gilb.* 20, 147.—Von Humboldt and Gay Lussac. *J. Phys.* 60, 129; also *Gilb.* 20, 129.—Berthollet. *Ann. Chim.* 53, 239; also *Gilb.* 20, 166.—De Marty. *Ann. Chim.* 61, 271; also *Gilb.* 28, 417; also *N. Gehl.* 4, 141.—Carradori. *Annali di Storia naturale di Pavia*, 5, 12, and 15; *J. Phys.* 62, 473; also *Gilb.* 28, 413: *Brugn. Giorn.* 6, 333.—Theod. de Saussure. *Bibl. Crit.*; also *Gilb.* 47, 163.—Thomson, *Système de Chimie trad. par Riffault sur la 5me edition*, 3, 61.—Graham, *Ann. Phil.* 28, 69.—Baumgartner. *Zeitschr. Phys. Math.* 8, 9.

Aqueous Solutions.

Gay-Lussac. *Ann. Chim.* 82, 171; also *Gilb.* 42, 117. *Ann. Chim. Phys.* 11, 296; also *Schw.* 27, 364; also *N. Tr.* 4, 2, 296.—Karsten, *Schriften d. Berl. Akad.* 1841.—Persoz, *Ann. Chim. Phys.* 63, 273; also *Ann. Pharm.* 33, 80.—Kopp, *Ann. Pharm.* 34, 260.

Peroxide of Hydrogen.

Thénard. *Ann. Chim. Phys.* 8, 306; 9, 51, 94, 314, and 441; 10, 114, and 335; 11, 85, 208; 50, 80; partly also in *Schw.* 24, 257; 65, 439; also *N. Tr.* 3, 1, 60, 72, and 80; 3, 2, 373, and 378; 4, 2, 37, and 40; also *Gilb.* 64, 1.—Compare also Thénard, *Traité de Chimie*, ed. 4, t. 2, 41.

Basis of Water, Hydrogène, Hydrogenium, Wasserstoff; and in the state of gas: *Hydrogen gas, Inflammable Air, Gas hydrogène, Gas hydrogenium, Wasserstoff-gas.*

History. Water was long regarded as an elementary substance. It was for some time supposed that by repeated distillation it could be converted into an earth; till Lavoisier showed that the earthy deposit in the glass distilling vessels proceeded from the glass itself. The inflammable air which is evolved during the solution of certain metals in dilute acids had been known for some time; and in 1781, Cavendish and Watt first showed that in the combination of this gas with oxygen, which takes place when it is burnt, water is produced. Subsequently, Lavoisier decomposed water into its elements. Von Humboldt and Gay-Lussac showed that one volume of oxygen gas combines with exactly two volumes of hydrogen gas to form water; whereas Lavoisier and Meusnier had found the ratio to be 12 : 23; Fourcroy, Vauquelin and Seguin, 100 : 205; and Nicholson and Carlisle, 72 : 143.—In 1818, Thénard discovered the peroxide of hydrogen.

Sources. Hydrogen is never found in the free state. The compound which contains it in the greatest abundance is water, of which it forms one-ninth. It occurs in smaller quanties in combination with phosphorus, sulphur, iodine, bromine, carbon, and nitrogen; and finally, in almost all organic compounds.—The gas which exists in a highly compressed state in the decrepitating rock-salt of Wielicska, and is set free with a decrepitating noise when the salt is dissolved in water, appears to be a mixture of hydrogen, carbonic oxide, and marsh-gas. (H. Rose, *Pogg.* 48, 353; *comp.* Dumas, *Ann. Chim. Phys.* 43, 316; also *Pogg.* 18, 601; also *Schw.* 59, 486).

Preparation. Always by decomposition of water.

1. It is obtained in the state of greatest purity by electric action: (a.) Berzelius conducts two brass wires connected with the poles of a voltaic battery, into water the conducting power of which has been increased by the addition of a little common salt.—(b.) A platinum wire is sealed into a glass tube, filled with water—to which a small quantity of some salt is added to make it a better conductor,—and inverted in a glass filled with the same liquid, into which the positive pole of a voltaic battery is made to dip, while the negative pole is connected with the wire fused into the tube.—(c.) Fuchs (*Schw.* 15, 494) inverts a platinum crucible in dilute hydrochloric acid, and places a zinc plate in connexion with its base: a considerable quantity of hydrogen gas then collects in the crucible.—(d.) Döbereiner (*Gilb.* 68, 55) puts a quantity of solution of sal ammoniac into a tube closed with a bladder at bottom and fitted with a gas-delivery tube at top; dips a platinum wire into the solution; immerses the whole in a vessel containing dilute sulphuric acid and a piece of zinc; and connects the zinc with the platinum wire.

2. Amalgam of potassium is placed, together with water, in a gas-generating vessel. The gas thus obtained is scentless; but it acquires the same odour as that evolved by zinc, if a little acid be added to the water. (Berzelius, *Lehrb.* 1, 147.)

3. Vapour of water is passed over finely-divided iron contained in a gun-barrel heated to bright redness. The middle part of the gun-barrel b (*App.* 42) contains iron nails or wire (filings alone would stop up the tube). When it is red hot, the water contained in the retort *a* is made to boil. The iron is converted into Fe^3O^4, but a great part of the water passes over undecomposed. (I., 125.)

4. Zinc or iron is dissolved in 1½ parts of oil of vitriol previously diluted with an eightfold quantity of water,—or in 2 parts of hydrochloric acid diluted with 4 parts of water. (Scheme 17.)

The gas obtained by the use of zinc may contain the following impurities: 1. Sulphurous acid, if this acid were present in the oil of vitriol employed.—2. Nitrous oxide or nitric oxide gas, if the oil of vitriol contains nitric oxide, nitrous acid, or nitric acid.—3. Carbonic acid, found by Donovan and also by the author, with a particular kind of zinc, but not in any other case.—4. Hydrosulphuric acid gas, if the zinc contains sulphide of zinc, or the oil of vitriol contains sulphurous acid, or if fresh oil of vitriol be added to the dilute acid already acting on the zinc and rising in temperature, without mixing it well with the rest of the liquid (Fordos and Gelis, *J. Pharm.* 27, 730).—5. Phosphuretted hydrogen gas, if the zinc contains phosphorus.—6. Arseniuretted hydrogen, if the zinc contains arsenic, or the oil of vitriol is contaminated with arsenious acid.—These impurities give the gas an unpleasant odour. To obtain it

free from this odour, it is necessary to use oil of vitriol not containing any compound of oxygen and nitrogen, and to pass the hydrogen through liquids which will absorb or decompose the adventitious gases.—Donovan (*Ann. Chim. Phys.* 2, 375; also *N. Tr.* 1, 2, 295) removes the carbonic acid and hydrosulphuric acid (and likewise the sulphurous acid) by means of aqueous solution of ammonia (or potassa), decomposes the phosphide and arsenide of hydrogen, which give rise to the phosphoric odour and cause the gas to burn with a green flame, by means of fuming nitric acid (on the evaporation of which, phosphoric and arsenic acid are obtained), and finally removes the nitric oxide gas which results from decomposition of the nitric acid, by oil of vitriol.—Berzelius (*Lehrb.* 1, 185) passes the hydrogen gas through two long tubes, the first containing linen saturated with solution of sal-ammoniac, which retains the arseniuretted hydrogen (likewise the phosphuretted hydrogen);—the second, fragments of hydrate of potassa, which takes up the hydrosulphuric acid (also the sulphurous and carbonic acids). According to Berzelius, the mere passing of the gas through solution of potassa or through a tube filled with fragments of hydrate of potassa renders it perfectly inodorous, while the potassa acquires a sharp, repulsive odour.—Dumas (*Compt. rend.* 14, 540) conducts the hydrogen gas through two U-tubes, each about three feet long, and filled with broken glass. The glass in the first tube is moistened with solution of nitrate of lead, which removes the hydrosulphuric acid; that in the second with sulphate of silver, by which the arseniuretted hydrogen is separated; then follows a third U-tube filled with fragments of pumice-stone saturated with strong solution of potassa. Finally, to render the gas anhydrous, it is passed through a tube filled with fragments of hydrate of potassa; then through another containing oil of vitriol or anhydrous phosphoric acid.

Hydrogen gas obtained by means of iron may contain the same impurities as that obtained by the use of zinc. But besides these it contains: 1. *Ferruretted* hydrogen gas (*vid.* Iron), to be removed by fuming nitric acid or solution of corrosive sublimate (Dupasquier, *Compt. rend.* 14, 511). 2. The vapour of an oily hydro-carbon, which is produced in greater abundance in proportion as the iron contains more carbon, and communicates a peculiar repulsive odour to the gas. This oil may be removed by passing the gas through alcohol, and the alcohol afterwards separated by water. (Berzelius.)

The gas obtained by the use either of zinc or of iron may be deprived of all odour in four and twenty hours, by means of moistened charcoal powder. (Döbereiner, *Schw.* 3, 377.)

5. By dissolving zinc in contact with iron, in caustic potassa. *The gas thus obtained is perfectly inodorous.* (Runge, *Pogg.* 16, 130.)

In whatever manner the gas may be prepared, it always, according to Bischof (*Kastn. Arch.* 1, 179), contains a small quantity of atmospheric air,—the chief cause of which impurity is, most probably, that the liquids used in its preparation contain air in solution. The nitrogen cannot be removed; but, according to Döbereiner (*Schw.* 42, 62), the oxygen may be separated by leaving the gas for a while in contact with spongy platinum, which causes the oxygen to combine with a portion of the hydrogen and form water.

Properties. Colourless gas.—Sp. gr. (I., 279). According to the latest determination by Dumas & Boussingault, it is between 0·691 and 0·695.—Hydrogen gas is therefore 14½ times lighter than air; hence it may be

used for inflating air-balloons. Soap-bubbles filled with it rise rapidly in the air. It escapes rapidly out of vessels with their mouths turned upwards, but slowly out of those which have their mouths placed in the reverse position. [For its refracting power, see Vol. I., p. 95.] Very inflammable, but does not support the combustion of other bodies. Inodorous, in the pure state; but as commonly obtained, it has a disagreeable smell. Small animals introduced into this gas die instantly. In man, the pure gas excites, after two inspirations, disagreeable sensations and loss of muscular power; when mixed with air, it may be breathed for a longer time (Scheele, Fontana, H. Davy). Its injurious action is merely negative; that is to say, so long as it is inhaled, oxygen gas, which is essential to life, is prevented from entering the lungs. The violent symptoms experienced by Cardone (*Quart. J. of Sc.* 20, 393) must have proceeded from impurities in the gas.

Combinations. The combination of hydrogen with other bodies is not attended with development of light and heat, excepting when it combines with oxygen and chlorine, that is to say, with the most highly electro-negative of all known substances.

Hydrogen and Oxygen.

A. Water. HO.

Sources. Diffused through the atmosphere in the form of vapour; also as rain, snow, spring-water, river-water, sea-water; as water of crystallization in many minerals; as a constituent of organic bodies.

Formation. The ponderable matter contained in one volume of oxygen gas is exactly sufficient to convert into water the ponderable matter in 2 volumes of hydrogen gas. The two gases may be mixed at ordinary temperatures, so as to produce *detonating gas;* but the oxygen and hydrogen will not, under these circumstances, combine together in the form of water. The combination may be brought about, slowly or rapidly, in the following ways:—1. By elevation of temperature.—2. By the electric spark.—3. By sudden pressure.—4. By platinum and other solid bodies. —5. By contact with organic bodies in a state of slow combustion.—6. By contact with water (?).

1′. Not only the flame of a burning body, but likewise the heat of a red-hot iron wire, or a coal, hot enough to exhibit a visible glow by daylight, is sufficient to induce the rapid combination.

2′. The smallest possible electric spark is sufficient to cause the mixture to take fire.—*Cavendish's Apparatus.* The electric spark excites combustion only in those parts of the mixture which it actually touches; but the heat excited by this combustion raises the temperature of the contiguous particles, and thus the combustion is propagated through the whole mass. But when the detonating gas is mixed with other gases which cool it down (p. 34), combination is limited to the small quantities of gas on which the spark exerts its direct action. Hence, 1 volume of detonating gas no longer takes fire by the influence of the spark when it is mixed with ½ a volume of olefiant gas, 1 volume of marsh-gas, 2 volumes of hydrochloric acid, 8 of hydrogen, 9 of oxygen, or 11 of nitrous oxide gas (H. Davy); similarly, when it is mixed with 1½ volume of cyanogen, 2 volumes of ammoniacal gas, 3 of carbonic acid, 4 of carbonic oxide, or 6 of nitrogen (W. Henry, *Ann. Phil.* 25, 426). One volume of detonating

gas mixed with $\frac{1}{4}$ of a volume of carbonic oxide may be exploded by the spark of a powerful Leyden jar, but not when it is mixed with $\frac{1}{2}$ a volume of the same gas. Similarly, of the following pairs of numbers, the first denotes the number of volumes, which, when added to 1 volume of detonating gas, still allows the explosion to take place; the second, the number of volumes which prevents it. Hydrosulphuric acid, $\frac{1}{4}$ and $\frac{1}{2}$; olefiant gas, $\frac{1}{2}$ and 1; ammoniacal gas, $\frac{1}{2}$ and 1; sulphurous acid, 1 and 2; carbonic acid, 2 and 3; carbonic oxide or hydrochloric acid, 3 and 4; hydrogen or nitrous oxide, 7 and 9; air, 10 and 12; oxygen, 12 and 14. The abstraction of heat cannot be the only cause which prevents the explosion; since the quantities required to prevent it are not in the inverse ratios of the specific heats of the gases. (Turner, *Ed. Phil. J.* 12, 311.)

3′. On rapidly compressing a quantity of detonating gas in an iron tube, combination took place, and the tube burst (Biot. *A. Gehl.* 5, 95; also *Gilb.* 20, 99). If, on the other hand, detonating gas contained in a tube sealed at the top and closed with mercury at the bottom, be sunk in the sea to the depth of 540 metres (295 fathoms), where the gaseous mixture is subjected to a pressure of 50 atmospheres, no combination takes place (De la Roche, *Schw.* 1, 172).—If two platinum wires are sealed into a strong glass tube, the tube filled with water acidulated with sulphuric acid, a manometer introduced to determine the pressure, then the tube sealed at the other end, and the water decomposed by the electric current, the detonating gas at length attains a tension of 150 atmospheres, and is therefore compressed into $\frac{1}{150}$ of its ordinary bulk,—and yet no recombination takes place. (Degen, *Pogg.* 38, 454.)

4′. *Platinum.*—If a platinum wire wound into a spiral form, and placed at the opening of a glass tube from which hydrogen gas is flowing, be gently heated, it will become red-hot and set the hydrogen on fire. On blowing out the flame so that the wire may cool down below redness, it soon becomes red hot again, and rekindles the gas with a slight detonation. (Palladium acts in a similar manner, but less strongly; whereas wires of gold, silver, copper, iron, and zinc produce no effect of the kind.) H. Davy.

Fine platinum wire wound into a spiral sets detonating gas on fire at a temperature even as low as 50° or 51° (Erman). When a wire of this description has been used in the lamp without flame (vid. *Alcohol*), it is found to be corroded at the part where it was red hot, appearing dull and of a blackish grey, and consisting of a net-work of thin fibres; such a wire placed in a mixture of air and hydrogen gas at temperatures between 37° and 50° (99° and 122° F.) becomes red hot at the corroded part. (Pleischl.)—Platinum wire $\frac{1}{10}$ of a millimetre in thickness, and wound into a spiral of 100 coils, requires, when new, a temperature of 300° to make it exert the peculiar water-forming action; but after several ignitions, it acts as low as 50° or 60°. After being immersed in nitric acid, either hot or cold, and then dried at 200°, it acts even at the ordinary temperature of the air, and becomes red-hot when a sufficiently strong current of mixed air and hydrogen is directed upon it. Sulphuric acid exerts an action similar to that of nitric acid, but weaker; hydrochloric acid, still weaker. This property imparted by acids is retained by the platinum wire for a few hours only, when it is exposed to the air; but if the wire be kept in a vessel, no matter of what description, it retains the same property for upwards of 24 hours. The wire loses this property if it be insulated by inserting it into a stick of sealing-wax, and immersing it for five minutes in insulated mercury, or if it be exposed for the same time to a current of dry air, or of dry oxygen, hydrogen, or carbonic acid.

Ammonia, potassa, or soda, on the contrary, does not deprive the wire of its peculiar power. (Dulong & Thénard.)

Platinum filings of medium size exhibit, when quite freshly prepared, the power of causing the formation of water, and become heated, though not quite to redness, when placed in detonating gas. They lose the power, however, in the course of an hour or two; but it may be restored by ignition and gradual cooling, or to a still greater degree by nitric or hydrochloric acid: in the latter case, the filings, if kept in a close vessel, retain their power for several days. When exposed to a current of air they lose their power, but not so quickly as the wire. Insulation has no effect on them. Platinum filings prepared under water exert no action at ordinary temperatures. (Dulong & Thénard.)

Extremely fine platinum foil newly beaten out, and crumpled together like the wadding of a charge (not smooth, or wound round a glass rod) explodes detonating gas at ordinary temperatures. It loses this property, however, by exposure to the air for a few minutes, but recovers it by ignition in a covered platinum crucible. If kept in a close vessel, it retains its power for twenty-four hours. But if it be merely taken out, unfolded, and crumpled together again, its power of causing explosion is gone; and it afterwards—like thicker platinum foil—requires to be heated to between 200° and 300°, before it will induce the formation of water; and even then, the combination takes place without explosion. (Dulong & Thénard.)

In order that a plate of platinum may effect the combination of detonating gas, its surface must be free from all impurities. *Prepared platinum plates* for this purpose may be obtained by the following process. (*a*.) Two plates of platinum are used as the electrodes of a powerful battery, and made to decompose dilute sulphuric acid of specific gravity 1·336, for the space of five minutes. The plate which forms the cathode exhibits but feeble action on detonating gas; and if the sulphuric acid is contaminated with metal or other impurities which deposit themselves on the negative electrode, it exerts no action whatever. But the plate which has conducted the positive electricity into the sulphuric acid acts very energetically. If then the two electrodes be fused into the upper part of a glass tube filled with dilute sulphuric acid, and inverted in that liquid—so that the detonating gas evolved from the liquid may surround the platinum plates—it will, when the action of the current ceases, gradually disappear. If the positive plate be taken out of the acid, washed with water, and immersed in detonating gas, it induces the combination of the oxygen and hydrogen, first slowly, then with continually increasing quickness, often becoming heated to redness, and (after from thirteen to forty minutes) causing the gas to explode. If no explosion takes place, and the gas is renewed as fast as it condenses, the action continually diminishes, and finally ceases: it continues longer, however, in proportion to the purity of the oxygen and hydrogen gases employed—longest, therefore, when the detonating gas has been obtained by electrolysis. Mere washing with water does not render the plate so active as immersion in water for a quarter of an hour; for by the latter treatment, the sulphuric acid still adhering to the plate is more effectually removed. If the plate be washed with water, then dried with linen, and then the washing and drying repeated, it will act in detonating gas with still greater quickness, in consequence of its dryness. If, after drying, it be heated to redness in the flame of a spirit-lamp, it will act equally well; but after stronger ignition in the flame of alcohol, urged by the blow-

pipe, its action is weaker: its power is likewise diminished if the alcohol contains any impurities, such as salts, or if it deposits soot. The prepared plate, if exposed to the air, loses its power in twelve hours at the utmost, but retains it for a week if kept in a sealed glass tube, for a still longer time if immersed in sulphuric acid or solution of potash, and for fifty-three days when kept in pure water; whereas, if the water has been left to stand in wooden vessels, the power is destroyed in forty hours. Moreover, a platinum plate which has been used as the anode in sulphuric acid of a greater or less degree of concentration than 1·336, or in aqueous solution of nitric, oxalic, tartaric, citric, or acetic acid, or of phosphate, chlorate, or nitrate of potassa, sulphate of soda, or sulphate of copper, exhibits equal activity. In hydrochloric acid it acquires less power, still less in carbonate of potassa or soda, and none at all in caustic potassa. (Faraday.)

(*b*.) A degree of activity equal to that produced by the electric method may be imparted to the plate by rubbing it while held in the alcohol flame with a piece of hydrate of potassa, keeping the fused deposit in the liquid state for two minutes, then holding the plate in water, and waving it about for five minutes, afterwards dipping it for one minute into hot oil of vitriol, and finally washing it for a quarter of an hour in pure water. Borax or carbonate of soda may likewise be used instead of hydrate of potassa. The following methods may also be used, but they are less efficacious. Fusion of borax or carbonate of soda on the plate, and washing with water, makes it moderately active. Merely heating the plate for a minute in oil of vitriol and then washing it with water makes it very active; but if the sulphuric acid be removed by ignition instead of by washing, it becomes inactive, because the acid leaves impurities behind it. Boiling with nitric acid, especially the concentrated acid, and then washing with water, produces a very active plate. Heating with dilute sulphuric, tartaric, or acetic acid is only occasionally efficacious, according to the nature of the impurities. Boiling in solution of potassa sometimes produces a very active plate, at other times, has no effect whatever, the result depending on the kind of impurities to be removed. A plate which is not rendered active by this method becomes so after subsequent scouring with emery and solution of potassa. Many plates become active by ignition in the flame of a spirit-lamp; others, not. Some which have been rendered active in the ordinary alcohol flame lose their power by ignition in the same flame urged by the blow-pipe; either because many of the impurities present become more firmly fixed by strong ignition, or because impurities are introduced from the flame itself, perhaps even carbide of platinum formed. Rubbing with emery and dilute sulphuric acid or solution of potassa, by means of a cork, makes the plate tolerably active; rubbing with wood-ash, with water and cork, with chalk and water, charcoal and water, or satin-paper and water, is less efficacious. (Faraday.)

Plates of platinum prepared according to the methods described in *a* and *b*, rub together in a peculiar way, and even after ignition are easily and uniformly wetted by pure water; when used as electrodes, they evolve gas at all points of their surface, none of which properties are possessed by ordinary platinum. By exposure to the air for four and twenty hours, the platinum loses these properties, but regains them after being gently heated. (Rock-crystal and obsidian, likewise, cannot be wetted uniformly till they have been treated with oil of vitriol and water, and then, after drying, with water again; they also lose this property after exposure to the air for 24 hours, or wiping with the cleanest linen.) Faraday.

Spongy Platinum, that is, platinum in the loosely coherent state in which it is obtained by gentle ignition of the ammonio-chloride (NH^4Cl, $PtCl^2$), induces, at ordinary temperatures, the combustion of hydrogen mixed with oxygen or atmospheric air—first the slow, then, when it attains a red heat, the rapid combustion. At or near 0°, the ignition of the platinum takes place more slowly than at higher temperatures. And even when a gaseous mixture contains hydrogen gas mixed with an extremely small quantity of oxygen, or oxygen mixed with an extremely small quantity of hydrogen, the presence of spongy platinum will cause the slow formation of water to go on, till the whole of the gas which is present in the smaller quantity is converted into water. (Döbereiner.)

To obtain spongy platinum of the greatest possible degree of efficiency, it is necessary to use very pure platinum. The foil or filings used (more particularly the latter) is first freed by concentrated hydrochloric acid from any iron which may be adhering to it (as the iron would otherwise be precipitated together with the ammonio-chloride of platinum, and weaken the igniting power), then boiled in strong nitric acid, and afterwards dissolved in aqua regia. The solution thus obtained is evaporated to the consistence of syrup,—mixed with strong nitric acid,—poured off from any insoluble matter that may remain—mixed in the cold with a small quantity of distilled water—precipitated by a concentrated solution of sublimed sal-ammoniac in pure water, which may be previously mixed with a little alcohol—the liquid poured off from the precipitated ammonio-chloride of platinum—and the precipitate repeatedly washed with cold distilled water: if it be not thoroughly washed, the spongy platinum obtained by igniting it is not of a whitish but of a blackish grey colour, and has but little power of inflaming the gas. It is likewise advantageous to give the precipitate one strong ignition after saturating it with alcohol of 80 per cent., and then wash it four times with water. Lastly, the precipitate is to be moistened with a small quantity of ammonia and then ignited again. Spongy platinum thus prepared is capable, even after the lapse of 12 days, of inflaming detonating gas at a temperature of 2·5°. (R. Böttger, *Schw.* 63, 370; 68, 390.) The sal-ammoniac used for precipitating the platinum solution must be sublimed, because that which has not been thus treated often contains fixed salts. It is better to wash the spongy platinum immediately after igniting the ammonio-chloride than to wash the latter before ignition. (Mohr.) Spongy platinum, which has been too strongly ignited, is incapable of producing explosion, but still induces slow combustion. (Dulong & Thénard.) For making the *platinum balls* already mentioned (p. 26) *meerschaum*, either natural or artificial, is preferable to clay. This substance is rubbed up with water into a stiff pasty mass, then mixed with ammonio-chloride of platinum, and the mixture formed into balls, small cups, &c., which are slowly dried and then ignited. (Döbereiner, *J. pr. Chem.* 17, 158.)

Spongy platinum, when exposed to the air, loses its power of inflaming detonating gas, sometimes in a few hours, sometimes not for several days (Döbereiner); not so quickly, however, as platinum foil or filings; more quickly in damp than in dry air; although moistening it with water, or passing aqueous vapour over it, does not sensibly diminish its power. (Dulong & Thénard.) When spongy platinum has been thus exposed to the air, and a stream of hydrogen mixed with air is directed upon it, the heat of the hand is often sufficient to excite the combustion. Even spongy platinum moistened with water or alcohol, (not that which has been moistened with nitrate of ammonia or caustic ammonia,) excites,

when introduced into detonating gas, a slow formation of water, which sometimes goes on for several hours. (Döbereiner.) The lost power is restored by ignition and cooling (Döbereiner); likewise by moistening with nitric acid, and drying at 200°: the power restored by the latter method is not destroyed by the action of potassa or soda. (Dulong & Thénard.)

Ammoniacal gas destroys the inflaming power; even a drop of solution of ammonia evaporating in the room is sufficient to produce this effect: hence, also, the neighbourhood of stables from which ammonia is disengaged, renders spongy platinum inactive. (Böttger.) Nitric acid vapour or chlorine restores the power which has been taken away by ammonia; and the spongy platinum, before it sets fire to the mixture of air and hydrogen, evolves fumes of the ammoniacal salt produced. Hydrosulphuric acid gas, the vapour of sulphide of ammonium, and more especially that of sulphide of carbon, destroy the inflaming power; and when thus destroyed, it cannot be restored by the action of nitric acid or chlorine, but only by the application of heat considerably below redness. (Schweigger, *Schw.*, 63, 375.) Since hydrosulphuric acid gas is sometimes evolved during the solution of zinc in sulphuric acid, its accidental presence in the detonating gas may destroy the power of the spongy platinum; ignition will, however, restore its activity. (Artus, *J. pr. Chem.* 6, 176.) Immersion for a time in carbonic or hydrochloric acid gas rather heightens the inflaming power of spongy platinum. (Döbereiner.)

A platinum ball kept over mercury becomes inactive in four-and-twenty hours. Immersed in a vessel filled with oxygen, hydrogen, carbonic acid gas, or air, it remains active: if left for five minutes in hydrochloric acid gas, it loses part of its power; still more in olefiant gas, or coal gas; and if immersed for the same time in sulphurous acid, hydrosulphuric acid, or ammoniacal gas, it becomes completely inactive. If moistened with water, its action on detonating gas is very feeble at first, but gradually increases as the water evaporates. A ball moistened with sulphuric, nitric, or hydrochloric acid, has no action on detonating gas. One that has been moistened with alcohol or ether acts slowly at first, but the action increases more rapidly than in the case of the ball moistened with water. (Turner.)

The spongy platinum used in Döbereiner's *Instantaneous Light Machine* loses its power from the following causes: 1. Fine particles of dust in the air leave their ashes upon it as they burn. 2. Sulphate of zinc carried forward by the hydrogen, forms on the spongy metal an alloy of zinc and platinum, by reduction of the zinc during the action of the burning hydrogen, whereby the spongy platinum becomes hard and somewhat malleable, and loses all its activity. The power may however be restored by heating the metal with oil of vitriol in a porcelain capsule, for a quarter of an hour, till the acid begins to evaporate, then boiling it well in water six times, till it no longer reddens litmus paper. Driving off the sulphuric acid by ignition destroys the power of the platinum; because the alkali, which the acid has taken up from the dish, remains on the metal in the form of a thin film. (Mohr, *Ann. Pharm.* 18, 55.)

Platinum-paper-ash. White bibulous paper saturated three times with solution of ammonio-chloride of platinum, and then burnt, leaves a delicate and finely divided residue of platinum of the form of the paper, which sets fire to a mixture of air and hydrogen gas, even more quickly than spongy platinum. (Pleischl.) Platinum thus prepared is very

active, and the more so, the greater its purity. If paper, three times saturated with solution of chloride of platinum be burnt, the ash will exhibit its power at temperatures nearly as low as — 20° (— 4° F.) : at this temperature, however, its action ceases altogether, but immediately recommences when the cooling is diminished. The ash retains its power after exposure to the air for a considerable time. If it should not exhibit its full power, it may be restored to its former state by boiling in nitric acid, and subsequent ignition at a tolerably high temperature. On surrounding a thermometer bulb with this ash, placing it in a perfect vacuum, and allowing a stream of hydrogen gas to flow upon it, no rise of temperature ensues; but if air be allowed to enter till the tension becomes equivalent to 1½ inch of mercury, the ash becomes red-hot when the hydrogen is directed upon it; although, in this case, the oxygen gas is 18 times more expanded than in common air. (De la Rivè & Marcet, *Ann. Chim. Phys.*, 39, 328.)

Platinum reduced to Laminæ. A mixture of the aqueous solutions of chloride of platinum and tartrate of soda is heated in a glass tube, 30 inches long and ¾ of an inch wide, till it begins to grow turbid, and then exposed to sunshine for several days. The greater part of the platinum is then reduced and deposited on the sides of the tube in thin dark-grey laminæ. The tube with the liquid is inverted in a vessel containing water, and then filled with hydrogen gas: by this treatment, the platinum acquires a silvery whiteness, and becomes easily separable from the tube by mechanical means. It possesses considerable inflaming power. (Döbereiner, *Schw.* 47, 133.)

Platinum-black. This name is given to platinum reduced from an aqueous solution in a very finely divided, perhaps amorphous state, and in the form of a delicate black powder. [For the several modes of preparing it, *vid.* Platinum.] It instantly sets fire to a mixture of air and hydrogen gas; but passes, in consequence of the ignition which it suffers at the same time, into a state resembling spongy platinum. Platinum-black when newly prepared absorbs with avidity a large quantity of oxygen gas from the air, but little or no nitrogen. Consequently, when introduced into pure hydrogen gas standing over mercury, it converts a considerable quantity of that gas into water, by causing it to combine with the oxygen which it has itself absorbed. On being subsequently exposed to the air, it becomes charged—provided its state of aggregation has not been too much altered by the previous ignition—with about as much oxygen gas as it contained before, and thereby regains the power of burning hydrogen: and thus the action may be several times repeated. 10 grains of platinum-black prepared with zinc condense 0·42 cub. in. of hydrogen gas; consequently must have absorbed 0·21 cub. in. of oxygen; 10 grains prepared with sugar condense 0·75 cub. in., and 10 grains prepared by E. Davy's process condense 1·10 cub. in. of hydrogen, and therefore the latter must have absorbed 0·55 cub. in. of oxygen gas. Estimating the specific gravity of platinum-black at 16·000, it will follow that 1 volume of platinum-black prepared by zinc absorbs 97 volumes; 1 volume of the same prepared by sugar absorbs 173 volumes; and 1 volume of that prepared by E. Davy's process absorbs 253 volumes of oxygen gas. It appears then that platinum-black absorbs oxygen and carries it over to combustible bodies. (Döbereiner, *J. pr. Chem.* 1, 114.—*Ann. Pharm.* 14, 10.) 10 grains of platinum-black introduced into hydrogen gas standing over mercury convert 0·98 cub. in. of it into water; must therefore have absorbed 0·49 cub. in. of oxygen. (W. Henry, *Phil. Mag. J.* 6, 364.) When

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platinum-black is digested in dilute hydrochloric acid, the oxygen which it holds combines with the hydrogen of the acid, and there results, partly bichloride of platinum, which remains dissolved, partly protochloride of platinum, which sticks about the substance and destroys its igniting power; digestion in caustic potassa will however render it active again. Ammoniacal gas instantly destroys the power of platinum-black; but it may be restored to its former state by the application of a gentle heat, or by lightly blowing hydrochloric acid gas upon it. (Döbereiner, *Ann. Pharm.* 1, 29.)

Iridium.—*Spongy Iridium,* obtained by ignition of the ammonio-chloride, becomes strongly heated in detonating gas and produces water, the action not being attended with explosion. (Dulong & Thénard.) It possesses greater igniting power than spongy platinum, and does not lose it so readily on exposure to the air: its power is however destroyed by ammonia. (Döbereiner.)—Iridium-black, prepared by exposing a mixture of sulphate of iridium and alcohol to sunshine, thoroughly washing the precipitate thus obtained with nearly boiling water, and then drying it at 100°, instantly sets fire to detonating gas. (Döbereiner, *Schw.* 63, 465.)

Spongy *Osmium* induces the formation of water at temperatures between 40° and 50°, and spongy *Rhodium* at 240°. (Dulong & Thénard.)

Palladium in the state of foil or filings behaves like platinum. Spongy palladium ignites detonating gas at ordinary temperatures. (Dulong & Thénard.) Palladium foil may be *prepared* in the same manner as platinum, either by the electric current in dilute sulphuric acid, or by heating in oil of vitriol (pp. 47, 48); in either case, however, the action of the acid must not be continued too long, or it may dissolve some of the palladium. (Faraday.) Pulverulent palladium obtained by ignition of the cyanide, becomes heated to redness in a stream of hydrogen gas and common air, and causes detonation: its action is however less powerful than that of spongy platinum; strongest when the palladium is placed in a hole in a piece of charcoal, and the hydrogen directed upon it. (Pleischl.) Palladium-paper-ash acts almost as strongly as platinum-paper-ash (p. 50), the more so in proportion to the purity of the palladium: it does not lose its power by exposure to the air, even for a considerable time. (De la Rivè & Marcet.)

Gold in thin leaves acts on detonating gas at 260°,—in somewhat thicker leaves, at 280°. Gold-dust precipitated from solution by zinc, and dried at a low temperature, does not act below 120°; but after ignition it acts at 55°. (Dulong & Thénard.) Gold leaf may also be made active by electricity, or by heating in oil of vitriol. (Faraday.) Gold-paper-ash does not act below 50°. (De la Rive & Marcet.)

Silver-leaf acts less powerfully than gold-leaf, but at temperatures below the boiling point of mercury. Silver in the pulverulent state, as precipitated from its solutions by zinc and ignited, acts at 150°. (Dulong & Thénard.) Silver cannot be prepared by the action of the electric current in dilute sulphuric acid, or by heating it in oil of vitriol. (Faraday.) Silver-paper-ash becomes red-hot in detonating gas at temperatures between 120° and 150°. (De la Rive & Marcet.) Silver reduced from its oxide by heating in an atmosphere of hydrogen, also requires an elevated temperature to make it act. (W. Ch. Henry.)

Copper reduced from the oxide of hydrogen, and heated in the air to 264°, while a stream of hydrogen gas is directed upon it, does not set fire to the gas, but merely becomes oxidated. At a higher temperature it becomes heated to redness, inasmuch as it continually gives up to the hydrogen the oxygen which it has previously absorbed, and takes up a fresh quantity of

oxygen; and the state of ignition continues, even after the supply of heat from without has been discontinued. Similar effects are exhibited by nickel and cobalt. Iron reduced from its oxide by hydrogen gas likewise induces the rapid combustion of the gas at the temperature at which the reduction takes place. Lead reduced by hydrogen has no action. Turnings of copper or iron, zinc foil, and charcoal, do not act upon detonating gas below the boiling point of mercury. (W. C. Henry.) Cobalt and nickel in mass act at 300°. (Dulong & Thénard.)

Charcoal (Sir H. Davy found that a feebly glowing coal induces slow combination), pumice-stone, porcelain, rock-crystal, and glass (compare the observation of Grotthuss and Davy, mentioned on page 25), act below 350°: the action of fluor-spar is very weak. Angular pieces of glass cause the formation of twice as much water in a given time as rounded pieces of equal surface. Mercury heated nearly to the boiling point does not appear to induce the formation of water. (Dulong & Thénard.)

Other gases mixed with the detonating gas hinder or completely stop the action of platinum and the other metals above named.

When one volume of detonating gas is mixed with different quantities of the following gases, and spongy platinum introduced into the mixture, the metal is found to produce its effect in the presence of 10 volumes of oxygen, hydrogen, nitrogen, or marsh-gas, and of 6 volumes of hydrochloric acid gas: on the contrary, the action is either prevented or very much retarded by 11 volumes of nitrous oxide, 3 volumes of carbonic acid, $1\frac{1}{2}$ volume of olefiant gas, 1 volume of cyanogen, or $\frac{1}{8}$ a volume of carbonic oxide. (W. Henry, *Ann. Phil.* 25, 426.)

In a mixture of 1 volume of detonating gas with 1 volume of carbonic oxide, hydrosulphuric acid, or olefiant gas, in which spongy platinum is inactive, Liebig's platinum-black instantly becomes red-hot, and produces rapid combustion. (W. Henry, *Phil. Mag. J.* 6, 364.)

In a mixture of 1 or 2 measures of detonating gas and 1 measure of carbonic oxide, spongy platinum produces slow condensation. A mixture of 1 volume of hydrogen gas with nearly 1 volume of carbonic oxide and 1 volume of oxygen is slowly but completely burnt by the action of a ball of platinum, and spongy platinum often causes it to explode. A mixture of 5 volumes of hydrogen gas, 1 volume of carbonic oxide, and 3 volumes of oxygen, is condensed more slowly than a mixture containing less hydrogen. In all these slow combustions, carbonic acid and water are produced together. When the mixture contains 1 volume of detonating gas and 1 volume of carbonic oxide, $\frac{5}{6}$ of the oxygen combines with the carbonic oxide, and $\frac{1}{6}$ with the hydrogen. The greater the quantity of carbonic oxide in the mixture, the greater is the quantity of carbonic acid produced; and the greater the quantity of hydrogen, the greater is the quantity of water produced.

In a mixture of equal volumes of detonating gas and olefiant gas, a platinum ball first condenses the detonating gas alone; with a larger proportion of detonating gas, more carbonic acid is produced, from combustion of the olefiant gas. In a mixture of hydrogen, carbonic oxide, olefiant, and oxygen gases, the hydrogen and carbonic oxide are oxidized by preference; and if the quantity of hydrogen be small, and that of oxygen insufficient, the olefiant gas is scarcely acted upon. In a mixture of 1 volume of detonating gas with from $\frac{1}{3}$ to 10 volumes of marsh-gas, a platinum ball condenses the first only; it is only when the quantity of detonating gas amounts to rather more than five times that of the marsh-gas, that a small quantity of carbonic acid is produced;—the carbonic acid is

produced in greater quantity when a larger proportion of oxygen is present, in which case the formation of carbonic acid may take place when the quantity of detonating gas is more than four times as great as that of the marsh-gas. (W. Henry.)

The action of a ball of platinum on detonating gas is not prevented by the addition of the largest quantities of hydrogen, oxygen, carbonic acid, nitrous oxide, or atmospheric air; in a mixture of $\frac{1}{7}$ of a volume of carbonic oxide with 1 volume of detonating gas it is tolerably good; with $\frac{1}{5}$ of carbonic oxide, very weak in the cold, good when the temperature is raised; and with $\frac{1}{3}$ of carbonic oxide, it is nothing in the cold, and very feeble even on the application of heat; with $\frac{1}{75}$ of a volume of sulphurous acid gas, the action is rapid at first, but ceases before the whole of the detonating gas is consumed; also with from $\frac{1}{37}$ to $\frac{1}{18}$ of sulphurous acid, the platinum acts quickly at first, but soon becomes inactive; when the quantity of sulphurous acid amounts to $\frac{1}{13}$, no action takes place, not even on warming. With $\frac{1}{59}$ of a volume of hydrosulphuric acid gas, the action is rapid at first, but ceases before the whole is consumed; with $\frac{1}{29}$ of a volume of the same gas there is a very slow, imperfect action; and with $\frac{1}{19}$, no action at all, not even on heating. With $\frac{1}{4}$ of a volume of hydrochloric acid gas, rapid, perfect action; with 3 volumes, slow, but still perfect action; with 5 volumes, very slight. With $\frac{1}{9}$ of a volume of ammoniacal gas, rapid action; with $\frac{1}{5}$, slow, but perfect; with $\frac{1}{3}$, none in the cold, strong at higher temperatures. In those cases in which the platinum was heated, it was brought to such a temperature as just to burn the hand. (Turner, *Ed. J. of Sc.* 12, 311.)

Prepared platinum foil acts as follows on one volume of detonating gas with various other gases. The smallest retarding action is exerted by nitrous oxide; then follows hydrogen, then nitrogen; then air and oxygen gas: in these cases, 4 measures of the gases just mentioned were mixed with 1 measure of detonating gas. Combination likewise takes place rapidly in presence of 4 measures of carbonic acid gas. Carbonic oxide in the proportion of from $\frac{1}{2}$ a volume to 4 volumes interrupts the action; the platinum plate, when taken out of the mixture, is found to act perfectly in pure detonating gas. In a mixture of 33 measures of detonating gas, 2 of carbonic oxide and 1 of oxygen, the action is slow at first, but afterwards increases, and after 40 minutes, explosion takes place. Sulphuretted or phosphuretted hydrogen in the proportion of from $\frac{1}{20}$ to $\frac{1}{16}$ of a volume stops the action completely; and the platinum is afterwards inactive, even in pure detonating gas. Vapour of sulphide of carbon likewise stops the action, without however depriving the platinum of its igniting power. In a mixture of one volume of detonating gas with $\frac{1}{99}$ of a volume of olefiant gas, slight action takes place after 50 minutes, and explosion after 85 minutes. When $\frac{1}{49}$ of a volume of olefiant gas is present, explosion takes place in two hours; but in a mixture of 1 volume of detonating gas, $\frac{1}{43}$ of olefiant gas, and $\frac{1}{14}$ of oxygen, no action is perceptible, even in 45 hours. Ether vapour interrupts the action, though not completely; the vapour of volatile oils exerts a still greater retardation. In these cases, the hydrogen alone is slowly burnt; the ether and oils remain unconsumed. The action of spongy platinum is similar to that of platinum foil. (Faraday.)

When hydrogen mixed with various other gases is directed in a stream through the air on spongy platinum, the following results are obtained: A mixture of 1 volume of hydrogen and 6 volumes of carbonic acid makes the metal red hot, although the same mixture does not take fire on

the application of an ordinary flame. A mixture of equal volumes of hydrogen and nitrogen causes the metal to glow. 3 volumes of hydrogen with 1 volume of carbonic oxide or olefiant gas produce no ignition. Hydrogen gas, charged with vapour of ether or volatile oils, makes the platinum red hot. Hydrogen gas produced from the decomposition of water by red-hot iron (p. 43, 3), even after it has stood over water for a week and has lost all its disagreeable odour, is not affected by either spongy platinum or prepared platinum foil; even a mixture of this gas with 3 measures of ordinary hydrogen gas and 2 measures of oxygen, is not affected by prepared platinum foil; possibly in consequence of the presence of carbonic oxide. (Faraday, *Experimental Researches in Electricity*, Series 6, p. 190; also *Pogg.* 33, 149.)

It is only impure olefiant gas that prevents the action of spongy platinum, not the pure gas which has been well washed with potash. On a mixture of detonating gas with a large quantity of olefiant gas, spongy platinum acts in a few minutes, but condenses only the hydrogen ; so that in this manner olefiant gas and hydrogen may be separated. Also the vapour of ether, rock-oil, and other volatile oils does not interfere with the action of spongy platinum on detonating gas : on the contrary, when ether is present, the spongy metal becomes so strongly heated that a small portion of the ether is burnt at the same time, and produces carbonic acid. (Graham, *N. Qu. J. of Sc.* 6, 354).

In a mixture of 1 volume of detonating gas and from $\frac{1}{30}$ to $\frac{1}{13}$ of carbonic oxide, prepared platinum foil produces a slight diminution of volume in the course of 24 hours ; spongy platinum causes a trifling diminution in five minutes, and a considerable decrease in two hours. When the mixture contains $\frac{1}{3}$ of its volume of carbonic oxide, the condensation is slower, amounting to only $\frac{1}{5}$ in a day : in this action there is always produced, together with a small quantity of water, a proportionally large quantity of carbonic acid. When 1 volume of oxygen is mixed with 2 volumes of hydrogen and 2 volumes of carbonic oxide, the latter takes up 8 or 10 times as much oxygen as the former. Consequently, carbonic oxide does not prevent the action of platinum, but only retards it, perhaps because it appropriates the oxygen to itself. On a mixture of 1 volume of detonating gas and $\frac{1}{37}$ of a volume of olefiant gas purified by potash, the prepared platinum plate acts in the first minute; in 10 minutes, $\frac{1}{5}$ of the gas is condensed ; in 15 minutes, $\frac{1}{3}$; the plate becomes heated far above the boiling point of water, and only $\frac{1}{12}$ of the mixture remains uncondensed. Even when the olefiant gas amounts to $\frac{1}{18}$, the action is perceptible in the first quarter of an hour, and complete in two days. The action of spongy platinum is not at all retarded, even by $\frac{1}{2}$ a volume of olefiant gas. In a mixture of equal volumes of olefiant gas and detonating gas, spongy platinum acts instantaneously, but condenses only half of the gas ; and none of the residual gas is absorbed by potash. With three measures of olefiant gas, spongy platinum produces no condensation till after some hours. A mixture of 1 volume of detonating gas, and even 20 volumes of olefiant gas is condensed by Liebig's platinum-black. In some of these cases, a very small quantity of carbonic acid is produced ; in others, none at all. All gases which retard or prevent the action of platinum, have themselves some degree of affinity for oxygen. (W. Ch. Henry.)

Of the various explanations which have been offered of this remarkable property of platinum and other metals, the following by De la Rive is by far the most probable. Platinum in the air or in oxygen gas becomes covered, even at ordinary temperatures, with a very thin film of platinous

or platinic oxide: at the same time, the hydrogen acting upon this oxide, even in the cold, reduces the platinum to the metallic state again, and forms water. Hence when oxygen and hydrogen act simultaneously on platinum, a continued series of oxidations and reductions takes place, as individual points of the metal come in contact, first with oxygen, and then with hydrogen. The platinum acts therefore as the carrier of the oxygen to the hydrogen, which gases cannot of themselves, by reason of their gaseous condition, act upon each other at ordinary temperatures. The rise of temperature which accompanies this transference accelerates the alternate oxidation and reduction of the platinum; and the metal ultimately becomes heated to redness, at which temperature it is capable of inducing the direct combination of the oxygen and hydrogen. This theory is supported by the following considerations. De la Rive has shown (I., 446, 447), that a platinum plate acting as anode in the decomposition of water, oxidates on the surface: also that the plate oxidates when exposed to the air; inasmuch as, when subsequently used as the cathode, it evolves less hydrogen at first than afterwards. Moreover, that when the current is made to pass through the water alternately in opposite directions, both platinum electrodes become covered with a fine dust of platinum, produced by repeated oxidation and reduction. The same phenomenon is apparent when combustion takes place on the surface of platinum. A spiral of platinum wire fixed at the end of a glass tube from which hydrogen gas issues into the air—so that the wire constantly remains at a red heat—becomes corroded and covered with a powder, which is first grey and afterwards black. The same effect is produced, but with greater rapidity, even in 48 hours, in the lamp without flame (*vid.* Alcohol). In consequence of the greater surface of platinum thus formed, the platinum acts more strongly, glows throughout a greater length, and much more brightly—as was first observed by Pleischl, and afterwards confirmed by De la Rive. The activity of platinum increases as its surface is more finely divided, because a more rapid oxidation is thereby brought about. Hence spongy platinum acts more strongly than platinum foil, and platinum-black most strongly of all. With the last, Döbereiner has actually observed a rapid absorption of oxygen to take place (p. 51). The behaviour of platinum-black with hydrogen gas and dilute hydrochloric acid leads to the same conclusion. It is true, on the other hand, that Matteucci and W. C. Henry observed that platinum foil and spongy platinum absorbed a small quantity of hydrogen gas and no oxygen; but the experiment was made with platinum already a little oxidated in the air, so that the oxide formed upon it condensed the hydrogen. Platinum foil prepared according to Faraday's method absorbs, according to De la Rive, no hydrogen gas but only oxygen. The oxygen does not adhere loosely to the platinum, but combines with it and forms an oxide; for, according to De la Rive, it cannot be removed by gentle rubbing with linen, but only by brisker rubbing or by boiling with an acid which dissolves the oxide. Superficial impurities in the platinum are injurious, because they render it less oxidable or less reducible. Platinum is more active than other metals, because, on the one hand, it has a greater tendency than gold, &c., to become covered with a film of oxide at ordinary temperatures—and on the other hand, the oxide of platinum gives up its oxygen to hydrogen and other combustible gases at lower temperatures than are required for the reduction of the more oxidable metals: consequently these latter require a higher temperature to make them act

(p. 52). This explanation is not indeed applicable to the case of non-metallic bodies; but these do not act till heated above 300°.

Other Explanations:—1. Platinum, by virtue of strong adhesive power, condenses oxygen and hydrogen gases on its surface (I., 26), and in this condensed state they are capable of combining. (Faraday and others.) As the temperature of the platinum rises, the condensation of the gases on its surface ought to diminish; whereas, in reality, the action increases in intensity as the temperature rises. 2 Platinum condenses the combustible gas on its surface in the form of an envelope; and in this condensed state, the gas is capable of combining with the surrounding oxygen at ordinary temperatures. (Fusinieri, *Giorn. di Fisica*, 1825, 8, 259.) 3. Dulong & Thénard discover a sort of connexion and opposition between the power of metals to induce combination, and that which they also possess when red-hot of decomposing ammonia. In platinum, which possesses the former power in the highest degree, the latter is least developed; iron, on the contrary, exhibits the first-mentioned faculty in the smallest, and the last in the greatest degree. 4. Döbereiner and Schweigger seek to explain the phenomena in various ways by reference to electrical relations.

Platinum Instantaneous Light Apparatus, or *Döbereiner's Instantaneous Light Apparatus.*—Hydrogen gas is generated in a glass vessel by means of zinc and dilute sulphuric acid, and, by opening a cock, made to flow in a fine stream on spongy platinum, which immediately becomes red hot and sets fire to the gas. (Döbereiner, *Schw.* 38, 326; 39, 159; 63, 468.—Pfaff, *Schw.* 40, 1.—Böttger, *Schw.* 68, 390.—Mohr, *Ann. Pharm.* 23, 228.)

5'. Various organic substances in the act of spontaneous decomposition give rise, under particular circumstances, to the combination of oxygen and hydrogen. Such are peas and spelt-corns kept under water out of contact of air till they have evolved gas,—peat-earth, and decayed wood (fermenting grape-juice produces no effect). These substances must be used in the moist state. If they come into immediate contact with detonating gas, they leave the hydrogen unaltered, and merely convert a portion of the oxygen into carbonic acid. If, on the contrary, they are placed beneath a layer of water above which the detonating gas is confined, or if they are tied up in damp linen or silk-gauze and suspended in the detonating gas, they induce, at temperatures near 22° (72° F.), a gradual condensation of that gas—or of a mixture of four measures of air and one of hydrogen—and consequent formation of water. At the same time, however, part of the oxygen is consumed in the formation of carbonic acid. Silk-stuff thoroughly boiled in water and wrapped up in gauze while wet, does not begin to condense detonating gas for a fortnight, after which interval, its decomposition begins; cotton enclosed in muslin acts still more slowly. If the putrefaction of these substances be prevented by the use of antiseptics—for example, if peat-earth be moistened with solution of common salt,—the power of condensing detonating gas is destroyed. The above-mentioned fermenting substances likewise condense detonating gas mixed with three times its volume of oxygen, hydrogen, nitrogen, or nitrous oxide gas; and in the case of the last-mentioned gas, they likewise set free a quantity of nitrogen. One-fourth of a volume of carbonic acid gas added to the detonating gas prevents the condensation, although carbonic acid introduced into pure detonating gas by the fermentation of the organic substances has no such effect. A mixture of 1 volume of detonating gas with $\frac{1}{3}$ of carbonic oxide and $\frac{1}{3}$ of olefiant gas suffers no con-

densation; but in a mixture of 1 volume of detonating gas, $\frac{1}{4}$ of a volume of olefiant gas, and $\frac{1}{4}$ a volume of marsh gas, condensation takes place. Detonating gas formed by mixing oxygen with hydrogen produced from the decomposition of water by red-hot iron suffers no condensation; and the same is the case even with detonating gas in which the hydrogen thus obtained is mixed in the proportion of 1 to 4 with hydrogen produced by the action of zinc. It appears, then, that these mixtures behave with fermenting substances in the same manner as with platinum; carbonic acid alone forms an exception, probably because it interferes with putrefaction. This condensation of hydrogen gas by bodies in a state of fermentation explains why the air contains no hydrogen, or at most $\frac{1}{1000}$ of it, although this gas is often evolved in the decomposition of organic substances, and the action of lightning does not appear sufficient to effect its complete removal. (Saussure, *N. Bibl. univ.* 13, 380; also *J. pr. Chem.* 14, 152.)

6'. Water placed in contact with detonating gas at ordinary temperatures, brings about its conversion into water, in the course of a few months, possibly because the oxygen and hydrogen are absorbed by the water, and thus enabled to act freely on one another. (Hooke and Orkney, *Gilb.* 20, 143; N. W. Fischer, *Scher. Ann.* 3, 123.) Water saturated with oxygen gas takes more hydrogen, and water saturated with hydrogen gas takes up more oxygen than ordinary water. (De Marty.)—Saussure, on the contrary, observed no diminution of volume in detonating gas left in contact with water, when the water had once taken up as much detonating gas as was necessary to saturate it (5·25 measures of the gas to 100 of water).

The rapid combination of oxygen and hydrogen is accompanied by a feeble light and great development of heat, and may serve to produce extremely high temperatures. When one of the gases flows into the other, merely a quiet, pale, reddish flame is produced where the gases come in contact; but when they have been previously mixed, the combination set up at one part is so rapidly communicated to the rest, in consequence of the intimate mixture of which gases are capable, that it appears to take place at the same instant throughout the entire mass. A violent detonation is likewise produced, in consequence of the great elasticity of the intensely white-hot aqueous vapour; and the containing vessel, unless possessed of more than ordinary strength, is broken to pieces.

The name of *Lumen philosophicum* is given to the noiseless flame of hydrogen gas, issuing from a tube into the air, and there set on fire: a glass held over it is quickly covered with water.

When a glass bell-jar, tube, or bulb, open at bottom, and either open or closed at top, is held over the *lumen philosophicum*, a continuous musical note is frequently heard. This is the *Chemical Harmonica*, first described by Lampadius and Mussin-Pouschkin. This sound, which is produced even when the tube is wrapped round with a cloth, and likewise above 100°, at temperatures therefore at which the water formed is in the state of vapour—also, though not so strongly, by other combustible gases, viz. carbonic oxide, olefiant gas, marsh-gas, sulphuretted hydrogen, arseniuretted hydrogen, and the vapours of alcohol and ether—is attributed by Faraday (*Ann. Chim. Phys.* 8, 363) to this circumstance, that a strong current of air is established within the tube (by which in fact the flame is elongated), and that small portions of air are thereby mixed with the hydrogen in such a manner, as to form small

quantities of detonating gas, which when set on fire produces slight explosions succeeding each other quickly and regularly.

If a tubulated glass jar be filled under water with hydrogen gas, the tubulure opened, and the gas set on fire there, it burns with a faint quiet flame; but on lifting the jar out of the water, a flame 8 inches high is produced, and is finally extinguished with a slight detonation, because the air which enters at the bottom becomes mixed with the last portions of hydrogen, and forms a detonating mixture. (Berzelius, *Lehrb.* 1, 195.)

A mixture of 2 volumes of hydrogen gas and 5 volumes of atmospheric air, produces a moderate detonation when set on fire, and bursts vessels which are not very strong. On filling an ordinary phial three parts full of hydrogen, and letting the rest of the water run out, so that the quantity of air introduced may not be sufficient for the complete combustion of the hydrogen, then holding the phial with its mouth downwards and setting fire to the contents, the combustion takes place slowly, proceeding from below upwards; and with a suitable form of the bottle, and a proper proportion of the mixed gases, a sound is produced similar to that of the *chemical harmonica*. (Geiger.)

Detonating gas, or a mixture of 2 volumes of hydrogen and 1 of oxygen, produces, when soap-bubbles, &c., filled with it are inflamed, an explosion more violent than that produced by any other gaseous mixture, and when exploded in the *Air-pistol*, propels the cork with immense force. If a pitch-bladder be blown with detonating gas to the capacity of 20 or 30 cubic inches by means of a common clay-pipe, then let fall from the pipe on a plate strewed with lycopodium, and from this slipped on to the left hand, it may be set on fire with the right hand, without shattering or in any way injuring the hand by the explosion; it should, however, be held at some distance from the body. (Böttger, *Ann. Pharm.* 33, 348.) When set on fire in a confined space, as, for instance, by the electric spark in *Volta's Eudiometer*, detonating gas burns without noise, and with a sudden flash: if the gases are contained in a strong glass globe, a dazzling light is produced (p. 30). A vessel is more easily shattered by the explosion of detonating gas, when the gas is set on fire in the middle, than when the combustion is made to commence near the stoppered opening. (Döbereiner, *Schw.* 63, 164.)

In *Newman's* and *Clarke's Oxy-hydrogen Blowpipe*, detonating gas, or a mixture of 9 measures of hydrogen and 4 of oxygen, is condensed to the amount of several atmospheres in a metallic reservoir, and made to flow from this through a narrow tube, at the end of which it is burnt. The flame burns with a feeble light, but excites the most intense heat yet produced by any means whatever. According to Clarke, a mixture of 4 volumes of oxygen and 9 of hydrogen produces the strongest heat, stronger than that obtained by the combustion of a mixture of oxygen with coal gas or olefiant gas. Pfaff recommends a mixture of 1 volume of oxygen and $2\frac{1}{2}$ of olefiant gas, or of oxygen and coal-gas; which, he says, gives at least as much heat as oxygen and hydrogen. If the condensation in the reservoir amounts to 10 atmospheres, the gas no longer takes fire with facility, probably because it is too much cooled by expansion as it flows out. (Parrot.) The communication of the flame to the gas in the reservoir takes place with so much the less facility, as the gas issues with greater rapidity, and the tube has less width and greater cooling power (p. 34). But since in an experiment of some duration, the tube becomes continually hotter, and the velocity of efflux

of the gas continually diminishes, there is considerable danger of the flame ultimately passing into the receiver, causing an explosion which may probably be attended with fatal consequences. This accident may be prevented, either by oil or water valves, or, according to the plan of Hemming and Bischof, by interposing between the reservoir and jet a brass tube, 6 inches long and $\frac{3}{4}$ of an inch wide, filled with very fine wires of equal length placed longitudinally, and forcibly pressed together by means of a strong conical wire rammed down the middle; so that the channels for the gas are made very narrow, and effectually prevent the recession of the flame, however slowly the gas may issue. This backward communication of the flame is, according to Pfaff, easiest with hydrogen gas, less easy with olefiant gas, and least of all with coal gas.

The apparatus invented by Hare, in which the gases are contained in separate vessels, and only brought together just before they are burned, is free from danger, but less powerful than the preceding. The gases, as they issue from the two reservoirs, are either made to enter a common tube, (which may be filled with wire, according to Hemming's plan,) and from this by a fine jet into the air, where they are burned (Hare); or the oxygen gas passes into the air through a narrow tube, surrounded by a brass cylinder, of a diameter rather greater than its own; and the hydrogen gas passes through the narrow space between the inner and outer tube (Daniell); or the two tubes by which the gases are conducted are placed nearly parallel with each other, at an angle of 5°, and deliver the gases by two apertures situated $\frac{1}{30}$ of an inch apart. (Rutter.) In all these cases, the stopcocks of the reservoirs containing the oxygen and hydrogen must be so adjusted that the gases may be delivered in the right proportion. If the flame should appear too large in consequence of an excess of hydrogen, the flow of that gas must be restricted till the flame just begins to contract.

The flame of the oxy-hydrogen blowpipe is very pale in itself, but diffuses a dazzling light as soon as any solid body is introduced into it. When the jet of gas, after being set on fire, is directed under water, it continues to burn below the surface of the liquid, in the form of a globe, and fuses and burns wires held in it.

In order to show that the water produced by the combination of oxygen and hydrogen gases weighs exactly as much as the sum of the quantities of the two gases consumed, Cavendish, Lavoisier, Monge, Fortin, Fourcroy, Vauquelin, Seguin, and others contrived the *Gasometer*, an apparatus in which hydrogen gas is made to flow into a glass globe filled with oxygen, and there set on fire, and the combustion kept up by constant renewal of the two gases. In Döbereiner's Spongy Platinum Gasometer (*Schw.* 42, 62), a glass globe containing spongy platinum is exhausted of air, and detonating gas contained in a reservoir allowed to enter in small quantities at a time, by proper regulation of the stopcocks: a quantity of water is thus formed in the globe.

Water produced by the combustion of hydrogen gas contains nitric acid, if the gas consumed contains nitrogen; and likewise (according to Saussure, *Ann. Chim.* 71, 282) ammonia, if the hydrogen is in excess.

Preparation of Pure Water. Rain or snow-water (especially the latter) collected in clean vessels is pure, with the exception of a small quantity of air. The water which falls at the beginning of a shower may contain dust previously diffused through the atmosphere, but not

that which falls afterwards. Rain or snow-water collected in the neighbourhood of the sea, may also contain hydrochloric acid. The assertion of Hassenfratz (*J. de l'Ecol. polyt. Cah.* 4, 570), that snow-water is richer in oxygen than water from other sources, has been disproved by Fabroni.

Careful distillation of spring or rain-water in metallic vessels (it is best to use a copper boiler with a head and condensing tube of copper or silver) purifies the water from fixed saline or earthy matters, which it may contain: *Distilled Water*. When the head and condensing tube are made of copper or tin, a small quantity of metal may be introduced into the water, if the apparatus has been previously used to distil an acid liquid. If the copper is soldered with lead, pure water itself will form oxide of lead with it. From glass vessels water extracts alkali, common salt, &c. From water containing hydrochlorate of magnesia in solution, hydrochloric acid may distil over, unless the boiler likewise contains hydrate of lime, which may also serve to retain the carbonic acid of the water. If, however, the water contains any ammoniacal salt, this may be decomposed by the lime, and then the distilled water will be contaminated with ammonia, and will require a second distillation with a small quantity of sulphuric acid to retain the ammonia. Sulphuric acid is also useful when the water contains any volatile salt of ammonia, the carbonate, for instance.

The only mode of freeing water from the greater part of the air, that is to say, the oxygen, nitrogen, and carbonic acid, which it contains, is by long continued boiling: *Thoroughly boiled Water*. Water thus treated must, while yet boiling hot, be passed, without coming into contact with the air, into vessels standing over mercury: this is the only way of preventing it from again becoming saturated with air.

Properties. Water solidifies in the form of ice between 0° and $-10°$ C. (32° and 14° F.) Ice belongs to the six-membered or hexagonal crystalline system. Double six-sided pyramid (Fig. 131), $r: r^3 = 80°$; six-sided prism, often shortened into a tabular form (Fig. 135); the same with its edges removed (Fig. 137); triangular prism; rhombic prism, (Fig. 61), $u': u = 120°$. (Smithson, *Ann. Phil.* 5, 340; Hericart de Thury and Clarke, *Ann. Chim. Phys.* 21, 156; Hessel, *Kastn. Arch.* 10, 299.) Ice has but one axis of double refraction, and this axis is perpendicular to the plates of ice as they form; sometimes the plates have rhombohedral summits projecting from them. (Brewster, Phil. Mag. J. 4, 245; also *Pogg.* 32, 329.) Hailstones also are sometimes crystalline. (Grotthuss, *Scher. Ann.* 2, 135.) Snow exhibits the form of regular hexagonal tables; frequently six of these tables, more or less elongated, are united in the form of a star. In the crystals of ice formed on windows, the primary form is often a six-sided prism of somewhat greater thickness. (Marx. *Schw.* 54, 426.) The specific gravity of ice is 0·950, according to Le Royer & Dumas; 0·9268, according to Osann (*Kastn. Arch.* 19, 95); 0·9180, according to Brunner; and 0·9184, according to Playfair & Joule. Ice is colourless and transparent, a slow conductor of heat, a non-conductor of electricity, and becomes electric by friction.

Ice melts and is converted into water at temperatures above 0° C., 0° R., or + 32° F. The specific gravity of water is 1·000. One Paris cubic foot of water at 8° C. weighs 70 pounds, 223 grains, old French weight; or, 1 cubic decimetre (litre), at 4·44° C. weighs 18827·15 grains.

poids de marc, or 1000 grammes (Lefevre-Gineau); 1 Rhenish cubic foot at 20° C. weighs 64·963 Cologne pounds (Schmidt); 1 English cubic foot at 13·2° C. or 55·8° F. weighs 998·74 ounces *avoirdupois*. (Robison.) 1 English cubic inch at 15·6° C. or 60° F. weighs 252·506 grains, (Shuckburgh, *Schw.* 11, 59.) 1 cubic centimetre at 4° C. weighs 1 gramme. (*Comp.* Weber, *Pogg.* 18,608, Kupffer, *J. pr. Chem.*, 22, 62.) Tables of the density of water at different temperatures have been constructed by Hällstrom (*Ann. Chim. Phys.*, 28, 56), and by Markiewiz, (Pogg. 19, 135). [See also Kopp's Table, Vol. I., p. 231.] Water is at its maximum density at a temperature of 4° C. (I., 225.) Water is slightly compressible, but only under very great pressure. According to Perkins (*Gilb.* 72, 173; *Ann. Phil.* 17, 135, and 222; *Pogg.* 9, 554), the compression produced by a pressure of 326 atmospheres amounts to 0·035, therefore by 1 atmosphere, to 0·000108; by 2000 atmospheres, to $\frac{1}{12}$; according to Oerstedt (*Ann. Phil.* 20, 236; *Schw.* 36, 332; 52, 9; *Ann. Chim. Phys.* 22, 192; *Pogg.* 9, 603), the compression produced by one atmosphere amounts to 0·000045; and up to 70 atmospheres, the compressibility increases in direct proportion to the compressing power; according to Canton, a pressure of one atmosphere produces a compression of 0·000044. (*Compare* also Pfaff, *Gilb.* 72, 161; Colladon & Sturm, *Ann. Chim. Phys.* 35, 113; also *Pogg.* 12, 39, and 161.) The sudden compression of water is accompanied by a flash of light.

Water boils—when the barometer stands at 28 Paris inches, or 29·8 English inches—at 100° C., 80° R., 212° F., 0° D., and when converted into vapour, takes up 1,700 times the space which it occupies when liquid. [For the refractive power, tension, specific gravity, and latent heat of aqueous vapour, see Vol. I., pp. 95, 262, 263, 279, 283, 285.] Water is tasteless and inodorous.

		Calculation.	Dumas.	Berz. & Dulong.		Vol.	Sp. gr.
H	1	11·11	11·11	11·1	Hydrogen Gas	1	0·0693
O	8	88·88	88·88	88·9	Oxygen Gas	0·5	0·5546
HO	9	100·00	100·00	100·0	Vapour of Water	1	0·6239

(H^2O = 2 . 6·2398 + 100 = 112·48. Berzelius.)

Decompositions. 1. By electricity, into oxygen and hydrogen gases. (I., 446—455.)

2. The alkali-metals at ordinary temperatures—carbon, the metals of the earths, and likewise molybdenum, chromium, uranium, manganese, zinc, tin, cadmium, iron, cobalt, and nickel, at a low red heat—and antimony, bismuth, lead, and copper, at a strong red heat—take up the oxygen of water and liberate the hydrogen in the form of gas. In presence of various acids, this decomposition of water is effected at ordinary temperatures, or a little above, by most of the earth-metals, as well as by manganese, zinc, cadmium, tin, iron, cobalt, and nickel.

3. Chlorine, under the influence of light, or at a red heat, combines with the hydrogen of water, and liberates the oxygen in the form of gas.

4. Both constituents of water enter into new combinations, when the water is brought in contact with phosphorus, chloride of phosphorus, phosphide of potassium, &c.

Combinations. A. *Definite Compounds, Hydrates:—*

a. With Simple Substances. The hydrates of chlorine and bromine, containing 10 atoms of water.

b. With Acids. *α.* The ***hydrates of the oxygen-acids*** generally contain as many atoms of water as their normal salts contain atoms of base; the water in these hydrates plays the part of a base, and must be regarded as *Basic Water* or *Water of Hydration.* Most of the acid hydrates are solid; those of sulphuric and nitric acid, liquid; the solid hydrates of this class melt on the application of heat, provided they do not decompose. The combination, which is often attended with considerable development of heat, is very intimate, so that most of these hydrates rather evaporate unaltered than part with their water. To this class belong, *e. g.* the hydrate of sulphuric acid, or oil of vitriol (HO, SO^3); the hydrates of the three phosphoric acids ($HO, aPO^5, -2HO, bPO^5, -3HO, cPO^5$). To detect and estimate the water in hydrates of this description, they are heated in contact with a known weight of oxide of lead, lime, &c., in excess; these substances retain the acid, and allow the water to escape.

β. Oxygen-acids containing Water of Crystallization. Many acids combine with a larger quantity of water than is necessary for the formation of hydrates, and form crystalline compounds in which one part of the water exists as *Basic Water*, the rest, in a state of less intimate combination, as *Water of Crystallization* or *Ice of Crystallization.* Crystallized sulphuric acid is $SO^3, 2HO$, or more correctly, perhaps, $HO, SO^3 + HO$, that is to say, a compound of the hydrate with water of crystallization. On the application of heat, the water of crystallization evaporates first, then the undecomposed hydrate. Besides the hydrate and the crystallized acid, sulphuric acid likewise forms other definite compounds with water.

c. With Salifiable Bases. *α.* The ***hydrates of the Salifiable Bases*** generally contain a number of atoms of water equal to the number of atoms of acid required to form a normal salt, so that the water in these compounds plays the part of an acid. All hydrates of bases are solid, and fusible at a red heat, provided they are not decomposed. These combinations also are very intimate; their formation is sometimes accompanied by development of light and heat; and many of them are undecomposible at a red heat. The combination of water with baryta and lime is attended with great development of heat; hydrate of lime (CaO, HO) parts with its water at a red heat; hydrate of baryta (BaO, HO) remains undecomposed even at a strong red heat; hydrate of potassa, or *lapis causticus* (KO, HO), vaporizes undecomposed at a red heat. To determine the water in these compounds, they are heated to redness in contact with a weighed quantity of ignited silicic or boracic acid in excess, which drives out the water.

β. Salifiable Bases containing Water of Crystallization. From the aqueous solution of several alkalis, compounds are separated which, besides water of hydration, likewise contain a definite quantity of less intimately combined water, or water of crystallization. These crystals fuse at a gentle heat, evolve the water of crystallization, and leave the hydrate behind. Crystals of potassa are composed of $KO, 5HO$ or $KO, HO + 4HO$; crystals of baryta, of $BaO, 9HO$, or $BaO, HO + 8HO$.

d. With Simple and Double Salts. These compounds, which, according to the nature of the salts and to external circumstances, may contain from 1 to 24 atoms of water to each atom of salt, are produced: 1. When the powdered anhydrous salt is mixed with the requisite quantity of water. The moist paste, which is a mechanical mixture of the salt and water, hardens to a dry solid body as the water passes into the state of chemical combination, the change being often accompanied by

perceptible rise of temperature. Anhydrous gypsum mixed with water forms a solid mass; anhydrous Glauber's salt becomes moderately heated when mixed with water; in the case of anhydrous sulphate of copper, the temperature rises, according to Graham, to 135°.—2. When the anhydrous salts, in the state of powder, are exposed to the air for a considerable time, they for the most part take from it their full amount of water of crystallization. Ignited carbonate of soda placed in a moist atmosphere recovers the whole of its 10 atoms of water (Hugh Watson, *Phil. Mag. J.*, 12, 130); sulphate of magnesia and sulphate of zinc take up 7 atoms of water; sulphate of nickel, 6 atoms; pyrophosphate of soda ($2NaO, bPO^5$), 10 atoms; but anhydrous Glauber's salt takes up no water from the air (Blücher, *Pogg.* 50, 541).—3. When the salts are suffered to crystallize from their aqueous solutions. The same salt may —according to the temperature and concentration of the solution—crystallize either with or without water, and in the former case with a greater or smaller number of atoms of water. The hotter and more concentrated the solution, the less inclination has the salt to take up water; on the other hand, the colder and more dilute the solution, the greater is the quantity of water which the crystals take up. Addition of oil of vitriol to the solution of the salt may likewise cause it to crystallize in the anhydrous state, or with a smaller quantity of water than otherwise. But with the different quantities of water, which vary, not by a gradual transition, but according to determinate numbers of atoms, the crystalline form and other properties likewise vary: thus, the hardness and density of a salt diminish as its quantity of water increases. Nitrate of strontia crystallizes in regular octohedrons not containing water, when its aqueous solution is evaporated at a high temperature; but when a more dilute solution is left to evaporate in the cold, the salt crystallizes in oblique rhombic prisms containing 5 atoms of water. Solution of borax evaporated at a high temperature yields regular octohedrons with 5 atoms of water; but when crystallized in the cold, it yields oblique rhombic prisms with 10 atoms of water of crystallization. The water of crystallization of salts must be carefully distinguished from their water of decrepitation (I., 14): the former exists in crystals according to a definite number of atoms, and with it the crystalline form and other properties are essentially connected; the latter is accidentally enclosed in the crystals in irregularly varying quantities; and the salt retains the same form, whether the quantity of water thus enclosed is great or small.

Salts containing water of crystallization lose it: 1. By heating. Most hydrated salts, especially those which contain large quantities of water, dissolve in their water of crystallization either wholly or in greater part when strongly heated; they pass into the state of *Aqueous Fusion.* The water then evaporates with ebullition, and brings the salt, if it be viscid, into a spongy state (borax, alum). Many salts thus de-hydrated melt again at a red heat; and with regard to these, the *Igneous Fusion* thus produced must be distinguished from the aqueous fusion. Other salts which contain less water, or are less soluble in it (bicarbonate of potassa, gypsum), are converted by heat into an opaque, friable mass, made up of the particles of the dry salt and the interstices previously filled with the water of crystallization—the change proceeding from without inwards, and not causing any alteration in the external shape of the salt. But few hydrated salts decrepitate when heated (I., 14).

2. *Efflorescent Salts* part with their water, even at ordinary temperatures, when placed in air of a certain degree of dryness, and are thereby

brought into the opaque friable condition just described. In this process, the affinity between the salt and the water is overcome by the affinity of heat for water, and by the adhesion of the air to vapour of water. The latter force is greater in proportion as the quantity of aqueous vapour already present in the air is less. The more strongly therefore the salt retains its water of crystallization, the dryer must the air be to cause it to effloresce. Hence, according to A. Vogel (*Schw.* 22, 160), crystallized sulphate of copper, which remains unaltered in air in its ordinary state, effloresces rapidly in a space filled with air, in which oil of vitriol, lime, chloride of calcium, or some other substance having a strong attraction for water is placed; because, by this means, the air is continually kept in a state of perfect dryness. Still more rapidly does the efflorescence take place in a space devoid of air, and containing some such substance which absorbs vapour of water with rapidity; because, by this absorption of the vapour as fast as it is formed, the pressure which that vapour would by its tension exert on the water still contained in the crystal is removed. When the temperature of the air is between 6° and 12° (42·8° and 53·6° F.), and the dew-point (*i. e.* the temperature at which the aqueous vapour in the air would condense) 3° or 4° (37·4° or 39·2° F.) below this temperature, carbonate of soda with 10 atoms of water does not effloresce. In air whose temperature is 14·4° (57·9° F.), Glauber's salt effloresces when the dew-point is at 9·4° (48·9° F.), and carbonate of soda when it is at 8·9° (48° F.). In air at 14·4°, with the dew-point above 10°, Glauber's salt does not effloresce. (Hugh Wattson, *Phil. Mag. J.* 12, 130.) Many salts effloresce only when their surface is injured, the efflorescence then commencing at the place at which the scratch is situated: carbonate, phosphate, and sulphate of soda may, when uninjured, be kept for years in an open dish without efflorescing. (Faraday, *Pogg.* 33, 186.)

3. Immersion of the hydrated crystals in liquids which do not dissolve the salt but attract the water, brings them into the opaque effloresced condition; *e.g.* protosulphate of iron immersed in oil of vitriol or in alcohol.

When a salt contains several atoms of water of crystallization, it sometimes happens that one atom is retained with much greater force than the rest. This more intimately combined water is distinguished by Graham, under the name of *Constitutional Water.* Sulphate of magnesia (MgO,SO^3+7Aq) loses 6 atoms of water at 132°, but the seventh not below 238°. It is probable that sulphate of magnesia forms a crystalline compound with 1 atom of water, and consequently, that this constitutional water is to be regarded merely as more intimately combined water of crystallization; just as the 5 atoms of water in octohedral borax are in a state of more intimate combination than the other 5 atoms likewise present in ordinary borax. (Gm.)

[*Definite compounds of water with organic substances* will be described under the head of *Organic Chemistry.*]

B. *Compounds in variable proportion, containing excess of water. Aqueous solutions.* Water takes up several elementary substances, as iodine, bromine, and chlorine, also the greater number of acids, the alkalis, many salts, both simple and double, and many organic compounds, into itself,—forming solutions which are concentrated or dilute, according to the relative proportions of the water and the substance dissolved. Aqueous solutions may be divided into those in which the dissolved substance is gaseous, and those in which it is either liquid or solid.

a. Water absorbs all *Gases.* Of some it absorbs a volume about equal to its own; of others less; of others, again, a much greater volume.

Volumes of different Gases absorbed by 1 *Volume of Water.*

Name of Gas.	Dalton.	W.Henry.	Saussure.	Davy.	
Terfluoride of boron	——	——	——	——	700. J. Davy.
Ammonia	——	——	——	670	780. Thomson.
Hydrochloric acid	——	——	——	480	516. Thomson.
Terfluoride of silicium	——	——	——	——	263. J. Davy.
Sulphurous acid	20	——	43·78	30	33. Thomson.
Oxide of chlorine	——	——	——	——	above 7. Stadion.
Cyanogen	——	——	——	——	4·5. Gay-Lussac.
Chlorine	about 2	——	——	——	
Hydroselenic acid	——	——	——	——	above 3. Berzelius.
Hydrosulphuric acid	1	1·08	2·53	——	3. Gay-Lussac & Thénard.
Carbonic acid	1	1·08	1·06	——	1·16. Cavendish.
Nitrous oxide	1	0·86	0.76	0·54	
Olefiant gas	0·125	——	0·155	——	
Phosphuretted hydrogen	0·125	0·0214	——	0·025	0·018. Gengembre.
Marsh-gas	0·037	1·014	——	——	
Oxygen	0·037	0·037	0·065	——	
Nitric oxide	0·037	0·050	——	0·10	
Nitrogen	0·025	0·0153	0·042	——	
Carbonic oxide	0·0156	0·0201	0·062	0·02	
Hydrogen	0·020	0·0161	0·046	——	

In performing these experiments, it is of the utmost importance to free the water completely from air by long-continued boiling (p. 61); because the greater the quantity of any other gas previously contained in the water, the less will it take up of the gas which is the subject of experiment; the gas must also be perfectly pure and in excess.

Gases which may be liquefied by strong pressure (I., 285) are more abundantly absorbed by water than those which are not condensable; the condensability, however, is not always proportional to the capacity of absorption; thus, hydrochloric acid is more difficult to condense, but much more readily absorbed than sulphurous acid. The chemical attraction between the water and the ponderable base of the gas is therefore an element in the determination of the result.

Whatever may be the external pressure to which a gas slightly absorbable by water is subjected, the water always takes up the same volume of it at the same temperature; consequently, the *weight* of gas absorbed will be twice as great under a pressure of two atmospheres, and only half as great under a pressure of half an atmosphere, as it would be under the ordinary atmospheric pressure. (W. Henry.) This law is only approximately true: under a pressure of 7 atmospheres, water absorbs only 5 times as much carbonic acid gas as it does under a pressure of one atmosphere. (Couerbe, *J. Pharm.* 26, 121.) With gases of which water absorbs more than one volume, the variation of solubility consequent upon increase or diminution of external pressure is not nearly so great. Increase or diminution of temperature, by which the volume of the gas is expanded or contracted, produces the same effect as diminution or increase of external pressure—so that the quantity of any given gas absorbed by water is greater at low than at higher temperatures.

When a mixture of two gases is exposed to the absorbing action of water, both are absorbed; but the quantity of each gas taken up is less than it would be if that gas alone were placed in contact with the water.

According to Dalton, the quantities of the individual gases absorbed are proportional to the solubility of each of them in the separate state,

and to the relative quantities of them present in the unabsorbed gaseous mixture. For example, air contains $\frac{21}{100}$ of its volume of oxygen, and $\frac{79}{100}$ of nitrogen; and since, according to Saussure, 1 volume of water absorbs $\frac{1}{16}$ of a volume of oxygen, and $\frac{1}{24}$ of a volume of nitrogen gas,—it follows that 1 volume of water will take from the air $\frac{21}{100} \cdot \frac{1}{16} = 0{\cdot}0131$ of a volume of oxygen, and $\frac{79}{100} \cdot \frac{1}{24} = 0{\cdot}0329$ of a volume of nitrogen, making together 0·046 of a volume. Hence, of 100 volumes of air absorbed by water, 28·5 are oxygen, and 71·5 nitrogen. This calculation is only approximately confirmed by experiment. According to Von Humboldt & Gay-Lussac, distilled water saturated with air yields, when boiled, a gaseous mixture containing 32·8 per cent. of oxygen: rain water yields 31·0, snow water 28·7, and the water of the Seine, from 29·1 to 31·9 per cent. Döbereiner found by repeated experiments (*J. pr. Chem.* 15, 286), that the air expelled by boiling from aërated water contained 33·3 per cent., or exactly $\frac{1}{3}$ of oxygen gas. The difference between the results of calculation and experiment seems to imply that the solubility of oxygen gas in water is rather greater, and that of nitrogen rather less, than Saussure's experiments show. (*Compare* Configliachi, *Schw.* 1, 151. Thomson, *J. Chim. Med.* 13, 57.)

When a mixture of two or more of the less soluble gases is placed in contact with water in a confined space, the relative quantities of the several ingredients undergo an alteration, unless the water absorbs all the gases in the proportions in which they are mixed. According to Dalton, the following law always holds good: Let A, B, C, . . . denote the volumes of the several gases in the original mixture; a, b, c, . . . the quantities remaining in the unabsorbed residue; w the volume of the water, and $\frac{w}{m}, \frac{w}{n}, \frac{w}{p}$ . . . . the relative volumes of the several gases which would be absorbed, if each of them were present by itself: then

$$A = a + \frac{w}{m} \cdot \frac{a}{a+b+c....}$$

$$B = b + \frac{w}{n} \cdot \frac{b}{a+b+c...}$$

$$C = c + \frac{w}{p} \cdot \frac{c}{a+b+c...}$$

$$\text{and } A+B+C...... = a+b+c.. + \frac{w}{a+b+c....}\left(\frac{a}{m}+\frac{b}{n}+\frac{c}{p}...\right)$$

The absorption of gas takes place the more quickly, the greater the external pressure, the lower the temperature, and the greater the number of points of contact: it is therefore accelerated by agitation. Whenever a gas is absorbed by water, heat appears to be set free: in the case of the more easily soluble gases, hydrochloric acid for instance, the temperature may rise above 100°; with carbonic acid, on the contrary, it never exceeds a quarter of a degree; and with the still less soluble gases it is wholly inappreciable.

The liquid formed by the absorption of a gas in water always occupies a greater volume than the water alone: its specific gravity is in most cases greater; more rarely, as in that of ammonia, less than that of pure water. The greater the density of a gas, the greater also is that of its aqueous solution. In this combination, the gas has lost its gaseous form and assumed that of a liquid: the combination may be regarded as that of a less volatile liquid with one possessing greater volatility. (Graham.)

The combination is destroyed: 1. By diminution of atmospheric pressure. —2. By rise of temperature.—3. By access of other gases.—4. By access of non-gaseous substances miscible with water.—5. By congelation of the water.—6. By peculiar mechanical conditions.

1'. Since, when a gas is rarefied 100 times, water takes up just as much of it by volume, but only $\frac{1}{100}$ as much by weight, as it would if the gas were under the ordinary atmospheric pressure,—it follows that, when water saturated with gas is placed under the receiver of the air-pump, the gas will escape as the air is rarefied. But the evolution of the gas is never complete; partly because it is impossible to produce an absolute vacuum, —partly because the affinity of the gas for the water ultimately gains the preponderance over its elasticity. In the case of the less soluble gases, this point is not attained for a considerable time; but with those which are easily soluble it is very soon reached,—so that, from aqueous solution of hydrochloric acid, for example, only a small portion of the hydrochloric acid can be removed by the air-pump, and then the remaining compound of the water with the acid evaporates unchanged.

2'. By elevation of temperature, the elasticity of the gas is increased and its absorbability diminished. In this manner, however, only a portion of the gas can be removed. But when the water ultimately boils, the attraction of the watery vapour for the gas (compare pp. 20 and 265, Vol. I.) seems to induce the latter almost entirely to abandon its state of combination with the liquid water, and escape in company with the aqueous vapour. Hence, by several hours' boiling, the less soluble gases and ammonia may be expelled from water, but not the other easily soluble gases, such as hydrochloric acid. Of this gas, a portion may be evolved at the commencement; but afterwards, the whole of the water and acid evaporate together as a chemically combined whole; and the remaining portion not yet evaporated is as rich in hydrochloric acid as that which has passed over. It is remarkable that nitrogen gas is much more easily separated from water by boiling than oxygen gas,—so that when water containing air is boiled and the air evolved is collected in separate portions, the first portions contain proportionally much less oxygen and more nitrogen than those which follow.

3'. When water saturated with a gas A comes in contact with another gas B, then, according to Dalton's law above given, the quantity of the first gas expelled and of the second absorbed will be such, that the volume of the gas A remaining in solution will be $\frac{w}{m} \cdot \frac{a}{a+b}$, and that of the gas B absorbed, $\frac{w}{n} \cdot \frac{b}{a+b}$. If both gases possess the same degree of solubility, so that $m=n$, the gas B, which is brought in contact with the water, will suffer no change of volume by being converted into a mixture of A and B: if, on the contrary, B is either more or less soluble than A, the gaseous mixture formed will be less or greater in volume than the gas B before mixture. When water saturated with any gas A is placed in contact with the open air, the whole of A is set free, while the water absorbs the constituents of the air. For if, as in the preceding formula, we express by a the quantity of the gas A which does not remain dissolved but escapes, and by b, c, d, the almost infinite quantity of the non-absorbed oxygen, nitrogen, and carbonic acid gases which constitute the common air, the fraction $\frac{a}{a+b+c+d}$ will be so extremely small, that when mul-

tiplied by $\frac{w}{m}$, it will give an almost evanescent value to the quantity of the gas A which remains absorbed by the water, when the liquid is exposed to the open air. On the contrary, when any gas confined within a limited space—under a bell-jar, for instance—is placed in contact with water containing air, it is in part absorbed by the water, while the oxygen and nitrogen gases contained in the water pass up into the bell-jar, and mix with the unabsorbed portion of the other gas. But inasmuch as motion is continually communicated to the water by agitation and change of temperature, by which fresh portions of aërated water are continually brought in contact with the confined gas, the water ultimately absorbs the whole of that gas, and discharges it into the air at another place, while the bell-jar becomes filled with the oxygen and nitrogen of the common air.

4′. On dissolving various salts in water containing any gas in solution, or adding oil of vitriol to it, &c., the absorbing power of the water is diminished, in consequence of the new combination into which it enters, and a portion of the dissolved gas is suffered to escape. One volume of Seine water, from which 0·018 of a volume of air and 0·003 of carbonic acid may be expelled by boiling, evolves, when mixed with 1 volume of strong solution of potassa, 0·017 of a volume of air. (Payen, *Ann. Chim. Phys.* 50, 303.) Water saturated with sulphate of magnesia absorbs only $\frac{1}{4}$ as much carbonic acid and $\frac{1}{3}$ as much hydrosulphuric acid as pure water; but on the other hand, water saturated with nitre or Glauber's salt absorbs as much of these two gases as pure water does.

5′. When water combined with a gas of which it can only take up its own volume at the utmost, is exposed to a degree of cold at which it freezes, the gas which it has absorbed is set free at the moment of solidification. On the contrary, the compounds of water with the more readily soluble gases freeze altogether, without allowing the absorbed gases to escape.

6′. When water containing any gas is subjected to a lower pressure or a higher temperature than that at which it was saturated, the portion of the gas which—according to what has just been explained—ought to be set free, does not always escape immediately. Its evolution is, however, accelerated either by agitation or by throwing in sand, silver-leaf, and other angular bodies, or by the immersion of glass rods, wires, &c.: the immersed bodies immediately become covered with gas bubbles. (pp. 270, 271, Vol. I.)

All compounds of water with gaseous bodies are to be regarded as chemical. Dalton supposes that gases of which water does not absorb at most more than its own volume, are only mechanically absorbed by it, so that the gaseous particles are distributed about in the pores of the water. (The various arguments which militate against this assumption I have put together in *Gehler's physik. Wörterbuch.* Ausg. 2. B. 1, S. 73.)

b. The *solution of liquid and solid bodies* in water is accompanied sometimes by development, sometimes by absorption of heat. According to Gay-Lussac (*Ann. Chim. Phys.* 70, 426), all salts, such as nitre, which are incapable of combining with water of crystallization, produce a fall of temperature when they dissolve; the others, on the contrary, such as anhydrous sulphate of soda, produce a rise of temperature; consequently, the latter must be supposed to dissolve in combination with their water of crystallization. Bodies which attract vapour of water from the air and dissolve in it are said to be *Deliquescent.* This deliquescing tendency varies with the temperature and hygrometric state of the air. (Gay-

Lussac, *Gilb.* 42, 246.) Many salts effloresce in dry and deliquesce in moist air*.

The density of a solution is generally above the calculated mean. The water in solutions is generally held by a much weaker affinity than that which exists in the combinations enumerated under the head A. Hence when the temperature is reduced below 0°, a part of the water or even the whole of it separates in the form of ice (I., 113). Most solutions have boiling points above that of pure water (I., 269). All salts may be completely dried at the temperatures at which their saturated solutions boil,—*e. g.* carbonate of potassa at 135°, chloride of calcium at 180°. (Legrand, *Ann. Chim. Phys.* 59, 429; also *J. pr. Chem.* 6, 59.)

It is remarkable that water dissolves but few simple substances, and these in small quantity only; that, on the other hand, it is most inclined to dissolve those compounds which contain one or both of its constituents (as is more particularly seen if we admit the conversion of haloid salts by water into hydrogen salts of metallic oxides); that it is chiefly through the medium of water that the acid reaction of oxygen-acids, and the alkaline reaction of the fixed alkalis is developed; that many bases which are insoluble in water have their alkaline reaction brought out by entering into some combination by which they are rendered soluble in water, *e. g.* protoxide of lead by combination with a small quantity of acetic acid, red oxide of mercury by combination with hydrocyanic acid. (*Comp.* Döbereiner, *Gilb.* 58, 213.)

With regard to the different quantities of a substance which water can dissolve at different temperatures, the following cases may be noticed:—

1. The same quantity is dissolved at all temperatures. Such, according to Fuchs, is the case with common salt.

2. The quantity dissolved continually increases with the temperature. In this case, which is by far the most common, the quantity taken up by the water is, according to Gay-Lussac, the same whether the water is agitated in contact with the substance till the point of saturation at the given temperature is attained, or the salt is dissolved in hot water and the solution left to stand till all the excess of salt is crystallized out. When water is saturated with a salt, especially carbonate of potassa, at the particular temperature at which the saturated solution boils, the liquid often remains at that heat for some time after removal from the fire; but as soon as the salt begins to separate, a constant and somewhat lower temperature is established. The most highly saturated solution of carbonate of potassa exhibits a temperature of 140°; on a sudden it froths violently up, deposits salt, and remains for some time at 135°. (Legrand.)

a. The solubility of the substance increases in direct proportion to the temperature. If we know the solubility of such a substance at 0°, and likewise the *additional* quantity which will be dissolved at a temperature of 1° higher, we have sufficient data for calculating the solubility at any other temperature. Thus, 100 parts of water at 0° dissolve 29·23 of chloride of potassium, and an additional 0·2738 for each additional degree of temperature. Hence, the solubility at 40° is equal to $29{\cdot}23 + 40 \,.\, 0{\cdot}2738 = 40{\cdot}18$. Similarly, with regard to sulphate of potassa, chloride of barium, and anhydrous sulphate of magnesia. (Gay-Lussac.)

* To free a gas completely from vapour of water it is usual to place within it some substance having a very strong attraction for water, *e.g.* hydrate of potassa, hydrate of soda, baryta, strontia, lime, oil of vitriol, phosphoric acid, nitrate of lime, acetate of potassa, chloride of calcium, nitrate or hydrochlorate of magnesia, burnt gypsum, &c.; or else a body which forcibly takes hold of the individual constituents of the water: *e.g.* gaseous fluoride of boron.

b. The solubility increases much more rapidly than the temperature, its increase being represented by a curve with its convexity downwards. This is the case with nitrate and chlorate of potassa and nitrate of baryta.

3. The solubility of the substance decreases as the temperature rises. This rare peculiarity is exhibited by lime, citrate of lime, butyrate of lime, and sulphate of cerium,—solutions of which substances saturated in the cold deposit part of the dissolved matter when the temperature is raised.

4. The solubility of the substance increases at first at a rapid rate as the temperature rises, as in 2, *b*; but reaches a maximum at a certain point, and diminishes from this point slowly and continuously, as the temperature is still further raised. 100 parts of water at 0° dissolve 12·17 parts of crystalized sulphate of soda; at 18°, 48 parts; at 25°, 100 parts; at 32°, 270 parts; at 33°, the maximum quantity, viz., 322 parts; and at 50·4°, 262·55 parts. (Gay-Lussac.) From the saturated solution at 33° (91·4° F.) hydrated salt crystallizes out on cooling,—anhydrous salt when the temperature is further raised.

When two salts, A, B, which neither decompose each other nor combine to form a double salt, are brought in contact with water at the same time, and in such quantities that a portion of each of them remains undissolved, the water dissolves a larger quantity of the whole than it would of either salt alone; and, according to Karsten, there are the three following cases to be considered:—

1. In the saturated solution of A, B, the water holds in solution a smaller quantity of A than it would if saturated with A alone; and less of B than if saturated with B alone. In this case there is a reciprocal partial separation: A added to the saturated solution of B separates a portion of B, and B added to the saturated solution of A separates a portion of A. But whether we proceed in the first way, or in the second, or add both salts in excess to the water at once, the quantity of each salt taken up by the water is invariably the same. Thus, sal-ammoniac added to a saturated solution of common salt separates a portion of that salt in cubes, and common salt added to a saturated solution of sal-ammoniac separates a portion of the sal-ammoniac in dendrites. At 18·75°, 100 parts of water dissolve 29·83 sal-ammoniac and 16·27 chloride of potassium, making together 46·1; the same quantity of water dissolves 22·05 sal-ammoniac and 32·64 common salt, making together 48·44; also 24·98 common salt and 52·82 nitrate of soda, making together 77·8. Similar relations are exhibited by sal-ammoniac with nitrate of ammonia or chloride of barium;—chloride of potassium with common salt or chloride of barium;—common salt with chloride of barium;—nitrate of ammonia and nitrate of soda appear likewise to act upon each other in a similar manner, excepting that the partial separation of the former by the latter does not take place till after several hours. When equal parts of the saturated solutions of sal-ammoniac and common salt are mixed together, no change of temperature takes place, but a mixture is formed capable of still dissolving both common salt and sal-ammoniac. When this mixture of two saturated solutions is heated in contact with common salt. it dissolves but a very small additional quantity of that substance; but when heated with sal-ammoniac, it dissolves the first portions clearly, without depositing anything; the solution of the following portions is accompanied by separation of common salt, the quantity thus separated increasing with the temperature: on cooling, the sal-ammoniac crystallizes out and the precipitated chloride of sodium redissolves.

2. The water dissolves the same quantity of the salt A, whether that salt is presented to it alone, or in conjunction with the salt B: on the contrary, it dissolves less of B when B is in conjunction with A, than when it is brought in contact with the water by itself. In this case, a one-sided partial separation takes place: A dissolves in the saturated solution of B in the same proportion as in pure water, causing a portion of B to crystallize out; but B dissolves in the saturated solution of A in smaller quantity than in pure water, without giving rise to the separation of any portion of A. In whichever order the process may be conducted, the same solution is obtained as when an excess of both A and B is placed in contact with water.

100 parts of water at 18·75° dissolve 33·07 chloride of potassium together with 1·79 sulphate of potassa, together = 34·86;—29·42 nitre with 4·00 sulphate of potassa, together = 33·42;—88·14 nitrate of soda with 3·77 nitrate of baryta, together = 91·91;—87·75 nitrate of soda with 34·26 nitrate of lead, together = 122·01. The following behave in a similar manner: chloride of potassium with sulphate or nitrate of potassa,—nitrate of potassa with nitrate of ammonia or sulphate of potassa,—common salt with crystallized sulphate of soda or sulphate of magnesia,—nitrate of soda with sulphate of soda, sulphate of magnesia, nitrate of baryta, nitrate of lead, or sulphate of zinc (excepting that in the last case, crystals double of sulphate of zinc and potassa are produced after a time),—nitrate of lead with nitrate of baryta. The first-named salt is in all cases the salt A, which dissolves in equal quantity whether the water is pure or already contains the salt B.

3. A given quantity of water dissolves more of the salt A when that salt is presented to it in conjunction with B than when it is alone, and at the same time also a larger quantity of the salt B. In this case, no precipitation takes place on adding B to the saturated solution of A; on the contrary, this solution, after B has been added to it, takes up a fresh portion of A; similarly when A is added to the saturated solution of B. In order, therefore, to obtain a constant proportion, both salts must be added to the water in excess.

It appears then that there are three kinds of saturation to be distinguished: (a.) The saturation by B of 100 parts of water already saturated with A.—(b.) The saturation by A of 100 parts of water already saturated with B.—(c.) The saturation of 100 parts of water by an excess of the two salts at once; in all cases at 18·75° (65·75 F.)

	a	*b*	*c*
A Sal-ammoniac	37·98	44·33	39·84
B Nitre	37·68	30·56	38·62
	75·65	74·89	79.46

	a	*b*	*c*		*a*	*b*	*c*
A Sal-ammoniac ..	38·04	38·6	39·18	Nitrate of potassa	29·45	33·12	38·53
B Nitrate of baryta	16·73	8·6	17·02	Common salt ..	38·25	36·53	39·19
	54·77	47·2	56·20		67·70	69·65	77·72
A Nitrate of potassa	29·45	35·79		Nitrate of potassa	29·9	53·04	59·2
B Nitrate of soda..	89·53	88·00		Nitrate of lead ..	84·1	51·56	109·8
	118·98	123·79			111·4	107·60	169·2

Similar relations are exhibited by sal-ammoniac with common salt or sulphate of potassa; nitrate of ammonia with nitrate of lead; sulphate of

potassa with sulphate of soda, common salt, or sulphate of magnesia (in the last case a double salt is formed); chloride of potassium with nitrate of baryta; nitrate of potassa with sulphate of soda; sulphate of soda with sulphate of magnesia or sulphate of copper (in which case a double salt is formed); nitrate of baryta with common salt or chloride of barium.

Solution of three Salts. From a saturated solution of sal-ammoniac and chloride of potassium together, the addition of common salt precipitates both sal-ammoniac and chloride of potassium: similarly, chloride of potassium added to a saturated solution of sal-ammoniac and common salt throws down a portion of both those salts. On adding nitrate of lead to a saturated solution of nitrate of potassa and nitrate of soda, the solution remains clear, and is no longer in a state of saturation: it contains in 100 parts of water, 134·38 nitrate of potassa and nitrate of soda, and 43·75 nitrate of lead, together amounting to 178·13. When fully saturated with all three salts, it contains 139·23 nitrate of potassa and nitrate of soda, and 53·24 nitrate of lead, making together 192·47. Similarly, a solution saturated with nitrate of potassa and nitrate of lead is not precipitated by nitrate of soda; and a solution saturated with nitrate of lead and nitrate of soda is not precipitated by nitrate of potassa. In both cases the solution is found to be unsaturated. Thus far, Karsten (*Schrift d. Berl. Akad.* 1841).

100 parts of water dissolve:

at 16·1°:	27·1 chloride of potassium	and 3·3 sulphate of potassa,	together	30·4
at 15·3 :	28·8 chloride of potassium	and 18·9 nitrate of potassa,	together	47·4
at 20·0°:	6·9 sulphate of potassa..	and 26·7 nitrate of potassa, .	together	33·6
at 16·8°:	27·7 chloride of potassium	and 18·2 chloride of barium,	together	45·9
at 21·5°:	33·1 nitrate of potassa ..	and 5·7 nitrate of baryta,..	together	38·8
at 20° :	59·5 nitrate of potassa ..	and 94·3 nitrate of lead,....	together	153·8
at 18·3°:	35·0 chloride of sodium ..	and 4·2 chloride of barium,	together	39·2
at 20° :	88·3 nitrate of soda	and 3·7 nitrate of baryta,..	together	92·0
at 20° :	84·6 nitrate of soda	and 38·4 nitrate of lead, ..	together	123·0

(Kopp. *Ann. Pharm.* 34, 260).

Nitrate of potassa dissolves more abundantly in water containing common salt or nitrate of lime than in pure water. (*Comp.* Longchamp, *Ann. Chim. Phys.* 9·5, also *N. Tr.* 3, 1, 209.) Gypsum dissolves more abundantly in water containing common salt than in pure water.

On the other hand, when a solution of nitrate of lime is mixed with a solution of nitrate of magnesia, a portion of the latter is precipitated (Dijonval); and according to Hermann (*Schw.* 47, 201), when a concentrated solution of chloride of calcium is mixed with solution of common salt, a portion of the common salt is separated.

B. Peroxide of Hydrogen. HO^2.

Oxygenated Water, Eau oxygenée, Deutoxyde d'hydrogène, Wasserstoff-hyperoxyd, Sauerstoff-wasser.

Formation.—When peroxide of potassium, sodium, barium, strontium, or calcium, is digested in any hydrated acid which forms a soluble salt with the salifiable base resulting from the decomposition of the peroxide, the excess of oxygen from the peroxide does not escape as gas, but passes over to a portion of the water, and converts it into peroxide of hydrogen. (Scheme, 105.) Thénard.

When black oxide of manganese purified by boiling water from

metallic chlorides, is mixed in a corked flask with ⅔ of its weight of fuming sulphuric acid and 6 times its weight of water, and the mixture left to stand, the watery liquid acquires an odour resembling that of chlorine, and the property of bleaching litmus. Peroxide of lead yields a liquid having still more powerful bleaching properties. (A. Vogel, *J. pr. Chem.* 1, 448.) Lampadius (*J. pr. Chem.* 17, 36) obtained a bleaching liquid with 1 part of peroxide of lead, ⅓ oil of vitriol, and 21 water, the mixture being put into a bottle, kept at 0°, and frequently shaken. (Oil of vitriol, even the fuming variety, may contain chlorine: *vid.* sulphuric acid.) According to De Marty, water saturated with oxygen gas still continues to absorb that gas when left in contact with it for a considerable time, so that in the course of a year and a half, it takes up half its volume of the gas: this effect may perhaps be attributed to the formation of a small quantity of peroxide of hydrogen. Paul succeeded by forcible compression in causing 2 volumes of water to take up one volume of oxygen gas.

Preparation.—Pure baryta is prepared by igniting in a porcelain retort nitrate of baryta free from iron and manganese. The baryta, broken into pieces about the size of a nut, is then put into a coated glass tube and heated to low redness, while a current of oxygen gas free from carbonic acid and dried by means of quicklime, is passed over it. For the first eight minutes the gas is eagerly absorbed by the baryta. After it has begun to escape from the farther end of the tube (to which a gas delivery-tube passing under water is fitted), the stream is still kept up for the space of ten or fifteen minutes. The peroxide of barium obtained by this process is, after cooling, preserved in a bottle. In the next place, 200 grammes of water are mixed with as much hydrochloric acid as will neutralize about 15 grammes of baryta. Into this liquid, contained in a cylinder, or better, in a dish of silver or platinum kept cool by surrounding it with ice, 12 grammes of peroxide of barium, slightly moistened and rubbed up in an agate mortar, are introduced by means of a wooden spatula: on agitating or stirring the liquid with the pestle, the whole dissolves completely and without effervescence. The baryta is next precipitated by oil of vitriol added drop by drop till slightly in excess: the presence of an excess of the acid may be known by the sulphate of baryta falling down more quickly than before. 12 grammes more of the peroxide are then dissolved in the same liquid, and likewise precipitated by sulphuric acid. The liquid, which now contains hydrochloric acid, sulphuric acid, a large quantity of water, and a small quantity of peroxide of hydrogen, is next separated by filtration from the sulphate of baryta, the precipitate washed with a little water, and the last wash-water retained for future washings. The filtrate is again mixed, as above, twice with peroxide of barium, and twice with sulphuric acid. The filtration is then repeated, and the process continued in the same way, till 90 or 100 grammes of the peroxide are consumed. The liquid thus obtained would, on decomposition, yield from 25 to 30 measures of oxygen gas. To separate silica, alumina, sesqui-oxide of iron, sesqui-oxide of manganese, &c., which proceed from the porcelain retort in which the nitrate of baryta was ignited, the liquid is mixed with concentrated solution of phosphoric acid (2 or 3 parts of phosphoric acid to 100 parts of peroxide of barium),—then surrounded with ice, and supersaturated with pounded peroxide of barium: silica and the phosphates of iron, manganese, and alumina then separate rapidly in flakes, and must be separated from the liquid by filtration

through linen, and if necessary, through paper. The presence of a large quantity of sulphate of baryta renders the filtration difficult. (If no phosphoric acid were present, the sesquioxides of iron and manganese would fall down by themselves, and give rise to a rapid evolution of oxygen gas; but when they are mixed with phosphoric acid, they do not produce this effect.) Should the liquid still contain portions of these oxides, they must be separated by the addition of a slight excess of baryta-water; whereupon, the liquid must be immediately and rapidly filtered through several filters at once, and the filters squeezed between linen to get all out. The whole of the baryta must then be separated by carefully adding sulphuric acid in very slight excess, and filtering. The filtrate now contains nothing but water, peroxide of hydrogen, hydrochloric acid, and a very little sulphuric acid. To separate the hydrochloric acid, the liquid is surrounded with ice, and mixed with sulphate of silver. In the first place, sulphate of silver, obtained by heating nitrate of silver in contact with oil of vitriol in a platinum crucible, is introduced in the form of powder into the liquid, —the whole being constantly stirred—till the liquid becomes clear, a sign that the hydrochloric acid is wholly or nearly precipitated. Any hydrochloric acid which may still remain must be separated by cautiously adding more sulphate of silver. If the latter has been added in excess, it must be precipitated by carefully dropping in a dilute solution of chloride of barium. The liquid should contain neither hydrochloric acid nor silver, and should therefore give no precipitate either with solution of silver or with hydrochloric acid. The chloride of silver is separated by filtration and pressure, any portion of liquid which comes through turbid being filtered over again. To remove the sulphuric acid also, and obtain a pure mixture of water and peroxide of hydrogen, the liquid is placed in a glass mortar surrounded with ice, and rubbed up with slaked baryta previously pounded and diffused through water: the baryta is added till the sulphuric acid is very nearly saturated. The liquid is then filtered, the filter pressed between linen, and baryta-water added in slight excess: this often occasions the precipitation of oxide of iron and oxide of manganese, as well as sulphate of baryta; hence the filtration must be rapidly performed. The excess of baryta is removed by cautiously adding dilute sulphuric acid, so that there may be rather a very slight excess of the acid than of the baryta. (The whole of the sulphuric acid may likewise be removed by means of carbonate of baryta obtained in a finely-divided state by precipitation, instead of by slaked baryta and baryta-water.) Finally, to separate the whole or nearly the whole of the water, the vessel containing the liquid is placed in a dish containing oil of vitriol, and the whole placed under the receiver of the air-pump: the water then evaporates before the peroxide of hydrogen. The fluid is agitated from time to time. If it should deposit flakes of silica, which give rise to the escape of oxygen gas, it must be decanted off from them by means of a siphon: if it should evolve oxygen,—which it will do as soon as it is so far concentrated as to contain about 250 times its volume of oxygen—two or three drops of sulphuric acid must be added to it. The concentration must be stopped after a few days, when the liquid is brought to such a state that when decomposed it would evolve 475 volumes of oxygen gas; for this residue, if left longer in vacuo, would evaporate as a whole. The peroxide of hydrogen must be kept in long glass tubes closed with stoppers and surrounded with ice; but, even under these circumstances, it decomposes slowly and evolves oxygen gas. (Thénard.)

2. Peroxide of barium is decomposed by hydrated hydrofluoric acid or

solution of hydrofluosilicic acid, the whole being kept constantly cool: in this case, insoluble fluoride of barium or double fluoride of silicium and barium separates at once. As soon as a sufficient quantity of acid and peroxide of barium have been mixed, the peroxide of hydrogen, still containing a large quantity of water, is filtered from the precipitate and concentrated in vacuo over oil of vitriol. (Pelouze, *Berz. Lehrb.* 1, 411.)

Properties.—Colourless, transparent liquid, of specific gravity 1·452; does not freeze at $-30°$ ($-22°$ F.); evaporates in vacuo at ordinary temperatures without decomposition, though much less readily than water; does not redden litmus, but gradually bleaches both litmus and turmeric paper; has a harsh, bitter taste, similar to that of tartar-emetic; whitens the tongue and thickens the saliva; when placed upon the hand, it instantly turns the cuticle white, and after a time produces violent itching. (Thénard.)

	Calculation.		Thénard.		Vol.
H	1	5·88	6·02	Hydrogen gas	1
2O	16	94·12	93·98	Oxygen gas ..	1
HO^2	17	100·00	100·00		

(H^2O^2 = 2 . 6·2398 + 2 . 100 = 212·48 . Berzelius.)

Decompositions.—The second atom of oxygen is retained by the hydrogen very loosely. Under various, and often enigmatical circumstances, it separates from the water in the form of gas, the volume of which at 14° (57·2° F.) and 0·76^m. bar. (29·8 inches) amounts to 475 times that of the liquid. The gas often escapes with such rapidity as to produce violent effervescence, and even explosion. Great *heat* is also developed, and when the experiment is made in the dark, even *light* is apparent (I., 234). The effect of explosion is most readily produced by oxide of silver, red or brown peroxide of lead, peroxide of manganese, osmium, platinum, and silver, the peroxide of hydrogen being suffered to fall in drops on these substances reduced to the state of extremely fine powder.

The several modes of decomposition are as follows:—

1. In the circuit of the voltaic battery, peroxide of hydrogen, like water, is gradually resolved into hydrogen at the negative and oxygen at the positive pole,—only that the proportion of oxygen is greater than in the decomposition of water. (Thénard.)

2. By a certain elevation of temperature. At freezing temperatures, peroxide of hydrogen is but very slowly decomposed; at ordinary temperatures, it merely evolves a bubble of hydrogen now and then, the decomposition not being complete for months; at 20° (68° F.) the escape of gas becomes more perceptible. By suddenly raising the temperature to 100°, this gradual escape of gas may be converted into a kind of explosion. Finally, there remains behind nothing but pure water. Sunshine does not appear to accelerate the decomposition at ordinary temperatures. (Thénard.)

3. By contact with certain substances, which either remain unaltered, or take up part of the oxygen of the peroxide, or on the contrary themselves evolve oxygen.—The rapidity with which these substances induce the separation of oxygen from the peroxide depends partly on their chemical nature, partly on the minuteness of their mechanical division: the further this is carried, the more rapid is the action. (Thénard. See I., 114, 115.)

a. Substances which induce the evolution of oxygen without themselves undergoing any alteration. The following act violently:—Charcoal (without formation of carbonic acid), silver, gold, platinum, palladium, rhodium, iridium, osmium. (Silver precipitated by zinc, and gold precipitated by protosulphate of iron, act with violence; silver in filings, slowly—in the massive state, very feebly; spongy platinum acts still more violently than precipitated silver or gold; a still more energetic action is produced by osmium;—on the other hand, spongy palladium, rhodium, and iridium, obtained by igniting the ammonio-chlorides, act somewhat less strongly than precipitated silver.)—A moderate action is produced by mercury, lead filings, finely pounded bismuth, powdered manganese; a very slight action by copper, nickel, cobalt, and cadmium. The following likewise induce violent decomposition: Sesqui-oxide and peroxide of manganese, sesqui-oxide of cobalt, massicot;—moderate decomposition is induced by hydrated sesqui-oxide of iron, the hydrates of potassa and soda (even when dissolved in water), hydrate of magnesia, and hydrated oxide of nickel;—a feeble action by sesqui-oxide of iron, oxide of nickel, protoxide of copper, oxide of bismuth, magnesia;—very feeble by black oxide of iron, sesqui-oxide of uranium, bi-oxide of titanium, sesqui-oxide of cerium, oxide of zinc, the hydrated peroxides of barium, strontium and calcium;—still more feeble by carbonate of soda, bicarbonate of potassa, protosulphate of manganese, sulphate of zinc, protosulphate of iron, and sulphate of copper; sal-ammoniac, the chlorides of potassium, sodium, barium, calcium, antimony, and manganese; and nitrate of manganese, nitrate of copper, subnitrate of mercury, and nitrate of silver. Rapid decomposition is likewise produced by fibrine of blood (which seems to undergo no change by the action—for it may be repeatedly used for the same purpose), and by the washed parenchyma of the lungs, nerves, and spleen (the oxygen set free by these animal structures is free from carbonic acid and nitrogen); whereas white of egg both liquid and coagulated, glue, and urea exert no decomposing action. (Thénard.)

b. Substances which not only separate oxygen from the peroxide, but at the same time give up their own oxygen and are reduced: Hydrated bi-oxide of platinum, oxide of gold, oxide of silver, protoxide of mercury (which are reduced to the metallic state), and the red and brown peroxides of lead (which are reduced to the state of protoxide). With all these oxides, the action is very violent. The reduction of oxide of silver takes place even with peroxide of hydrogen considerably diluted with water. (Thénard.)—For the cause of the reduction, see Vol. I., p. 115. Thénard and Mitscherlich (*Pogg.* 55, 321) regard it as a consequence of the development of heat.

c. The following substances, while they allow a certain portion of oxygen from the peroxide of hydrogen to escape as gas, absorb the remainder, and are converted into the following compounds:—Selenium into selenic acid (with great development of heat, but without light); potassium or sodium into potassa or soda (with combustion, evolution of oxygen gas, and often explosion); arsenic into arsenic acid; molybdenum into molybdic acid (these two with violent action and combustion: dilute peroxide of hydrogen dissolves arsenic, and converts it into arsenic acid without effervescence); tungsten into tungstic acid (moderate); chromium into chromic acid; zinc into oxide of zinc (very feeble); hydrate of baryta into hydrated peroxide of barium; hydrated protoxide of copper into the yellow hydrate of a higher oxide; hydrated protoxide of manganese into the hydrated peroxide; hydrated pro-

toxide of cobalt into hydrate of the sesqui-oxide; hydrated protoxide of iron into hydrate of the sesqui-oxide; arsenious acid into arsenic acid; sulphide of arsenic and sulphide of molybdenum (with violent action, even producing light) into sulphuric acid and arsenic or molybdic acid; sulphide of antimony, lead, iron, or copper, with great rise of temperature, into the sulphate of the corresponding oxide (sulphide of bismuth and bisulphide of tin act very feebly; protosulphide of mercury and sulphide of silver, not at all); kermes mineral and hydrated protosulphide of iron, with violent action, into the corresponding sulphates; and in a similar manner, iodide of barium, probably, into iodate of baryta.

d. The following substances take up the whole of the second atom of oxygen from the peroxide of hydrogen, without setting any of it free, and are thereby converted into the following compounds: Sulphurous acid into sulphuric acid; aqueous solution of hydrosulphuric acid, slowly into water, sulphur, and a very small quantity of sulphuric acid; aqueous hydriodic acid into water and iodine; baryta, strontia and lime dissolved in water into the corresponding hydrated peroxides, which are precipitated; hydrated protoxide of tin into hydrate of the bi-oxide.

In contact with vegetable substances, such as oxalate of potassa, acetate of potassa, alcohol, camphor, olive oil, sandarac, woody fibre, starch, gum, common sugar, manna-sugar, and indigo, the peroxide of hydrogen does not evolve oxygen perceptibly faster than when kept by itself; but the gas, at least when starch or sugar is present, is mixed with carbonic acid.

The following are destitute of decomposing action:—Antimony, tellurium, tin, and iron; alumina, silica, tungstic acid, sesqui-oxide of chromium, sesqui-oxide of antimony, antimonious acid, and bi-oxide of tin; phosphate of soda; sulphate of potassa, soda, baryta, strontia or lime; alum, mineral turbite, chlorate of potassa; nitrate of potassa, soda, baryta, strontia, or oxide of lead; chloride of zinc, corrosive sublimate, and bichloride of tin. (Thénard.)

Combinations.—*a.* Peroxide of hydrogen is miscible in all proportions with water. From this mixture part of the water freezes out when exposed to cold. The same circumstances which induce the decomposition of pure peroxide of hydrogen, likewise bring about the decomposition of that which is diluted with water; the action is, however, less violent, never attended with development of light, seldom with evolution of heat, and is not so soon completed. A mixture containing eight times its own volume of oxygen gas, begins to evolve gas at 50° (122° F.), and subsequently gets into a state of violent ebullition; and when this has ceased, nothing is left but water. (Thénard.)

b. Peroxide of hydrogen combines with hydrated acids; *e. g.* the phosphoric, sulphuric, hydrochloric, hydrofluoric, nitric, oxalic, citric, and acetic acids, forming compounds in which it is less easily decomposible than when alone. In these compounds, the acid was at first regarded as existing in a higher state of oxidation. The comparatively weak carbonic and boracic acids do not give stability to peroxide of hydrogen. The compounds of peroxide of hydrogen with acids are obtained either by direct mixture of the acid and the peroxide, or by dissolving the peroxide of barium in a hydrated acid and precipitating the baryta by cautiously adding sulphuric acid,—or by decomposing the compound of hydrochloric acid and peroxide of hydrogen, by adding to it the silver-salt of that acid which is to be made to combine with the peroxide of hydrogen. The

evolution of oxygen gas from these mixtures takes place less easily and more slowly than from the pure peroxide of hydrogen; but when the acid is neutralized by an alkali, the former facility of decomposition is restored. The greater the quantity of acid mixed with the peroxide, the more does the affinity of the acid for that compound interfere with its decomposition by elevation of temperature, or by contact with most of the bodies above mentioned. If either of the acids just enumerated be added to peroxide of hydrogen which has begun to evolve gas, the escape of gas ceases; it recommences at a higher temperature, but the whole of the oxygen is not driven off, even by half an hour's boiling. It is remarkable that although gold decomposes the pure peroxide much more rapidly than bismuth does, yet the quantity of acid required to stop the action of the gold is smaller than that which must be added to prevent the action of the bismuth. Peroxide of hydrogen, brought into a state of effervescence by gold, palladium, or rhodium, is restored to tranquillity by the addition of a single drop of dilute sulphuric acid. Ter-oxide of gold liberates oxygen gas from acidulated peroxide of hydrogen, and is itself reduced, first to the state of purple oxide, then to the metallic state. In the nitric acid compound of peroxide of hydrogen, oxide of silver is reduced, with evolution of oxygen; but part of the oxide dissolves in the acid. In the hydrochloric acid compound, the oxide of silver is converted into a violet-coloured chloride containing less than one atom of chlorine for each atom of silver. Peroxide of manganese, and likewise the red and brown peroxides of lead, liberate oxygen from sulphate, hydrochlorate, or nitrate of peroxide of hydrogen, and at the same time give up part of their own oxygen, so that a salt of protoxide of manganese or protoxide of lead is formed. In these acids combined with peroxide of hydrogen, many metals dissolve quietly, taking oxygen from the peroxide, thereby converting that compound into water, and being themselves brought to the state of oxides which dissolve in the acids. (Thénard.)

C. *Suboxide of Hydrogen ?*

Water absorbs only $\frac{1}{64}$ of its bulk of hydrogen gas, according to W. Henry; $\frac{1}{40}$, according to Dalton; and $\frac{1}{33}$, according to Saussure. Paul, however, asserts that by strong pressure, 1 volume of hydrogen gas may be forced into 3 volumes of water; and De Marty found that water may, by degrees, be made to take up a greater and greater quantity of hydrogen (the quantity taken up in two years being not quite equal in volume to the water itself); there may then exist a suboxide of hydrogen, H^2O. This compound may, according to Kastner (*Berl. Jahrb.* 1820, 472), be obtained by repeatedly saturating water, in the cold, with hydrosulphuric acid, and then removing the sulphur by means of certain metals.

Other Compounds of Hydrogen.

A. Hydrogen forms 10 inorganic *Hydrogen-acids*, or *Hydracids*, namely, the Hydrosulphurous, Hydrosulphuric, Hydro-sulpho-carbonic, Hydroselenic, Hydriodous, Hydriodic, Hydrobromic, Hydrochloric, Hydrofluoric, and Hydrotelluric acids. The first nine may be called *Mineral* or *Non-metallic Hydrogen-acids*, and thus distinguished from the last, which is a *Metallic Hydrogen-acid**. The inorganic hydracids always

* Many chemists, in accordance with the idea of Sir H. Davy, regard the hydrogen in hydracids as the acidifiable basis, and on the contrary, the sulphur, selenium, iodine, chlorine, &c., as the acidifying principle—a view of the matter which appears to be

contain one atom of hydrogen, and one atom, rarely more, of the acid-radical.

Respecting the action of hydrogen-acids on salifiable metallic oxides, two views are entertained (*vid.* pp.10....13). According to the second of these views, they form hydrogen-salts; according to the first, double decomposition takes place, and the metal combines with the radical of the acid. (a.) When a hydrogen acid comes in contact with a metallic oxide, in such proportion that the hydrogen of the acid exactly corresponds with the oxygen of the oxide—then, according to the second view, a normal hydrogen-salt is formed: *e. g.* KO, HS and $SnO^2, 2HS$; according to the first view, the elements interchange in such a manner as to form water, and a compound of the metal with the radical of the acid: *e. g.* $KS + HO$ and $SnS^2 + 2HO$. (b.) If the number of atoms of hydrogen in the hydracid exceeds the number of atoms of oxygen in the oxide, then, according to the second view, an acid hydrogen-salt is formed: *e. g.* $KO, 2HS$; according to the first view, there is produced, besides water, a compound of the metal with part of the radical of the acid, and this compound enters into combination with the rest of the hydracid: *e. g.* $KS, HS + HO$. (c.) When the number of atoms of oxygen in the metallic oxide is greater than the number of atoms of hydrogen in the hydracid, a basic hydrogen-salt is formed, according to the second view: *e. g.* $4CuO, HCl + 3Ag$; according to the first view, water is produced, and likewise a compound of the metal with the radical of the acid, and with this compound the undecomposed portion of the metallic oxide enters into combination: *e. g.* $3CuO, CuCl + 4Ag$.

B. Hydrogen forms one salifiable base, viz. *Ammonia*.

C. The remaining inorganic compounds of hydrogen take the form either of combustible gases, as Phosphuretted, Arseniuretted, and Antimoniuretted Hydrogen gas, or of solid bodies, as Hydride of Potassium, and Hydride of Arsenic.

In the gaseous compounds of hydrogen, the following relations of volume are found: (*a.*) One volume of the stronger hydracids contains half a volume of hydrogen gas: HF, HCl, HBr, HI. (*b.*) One volume of the weaker hydracids contains 1 volume of hydrogen gas: HS, HSe, HTe. (*c.*) One volume of those hydrogen compounds, which are more or less basic, contains $1\frac{1}{2}$ volumes of hydrogen gas: NH^3, PH^3, AsH^3. (I., 66.)

D. Hydrogen forms an essential constituent of nearly all organic compounds.

sanctioned by the electro-chemical theory. Since, however, sulphur, selenium, iodine, chlorine, &c., are not capable of forming well-defined acids with any substance excepting hydrogen or oxygen (p. 3),—for the fact that phosgene and pentachloride of phosphorus have been observed to redden litmus may be attributed to the presence of a trace of water,—and since hydrosulphuric and hydriodic acids possess stronger acid properties than the hydrosulphurous and hydriodous, which contain less hydrogen in proportion, it appears to me to be simpler to seek the cause of the acid nature of the compounds in question in the hydrogen which they contain.

Chapter III.

CARBON.

Lavoisier. Formation of Carbonic acid. *Crell. Ann.* 1788. 1, 552; 2, 55.
Cruikshank. Compounds of Hydrogen and Oxygen with Carbon. *Scher. J.* 7, 371.
Tennant. Nature of the Diamond. *Scher. J.* 2, 287.
Mackenzie. Combustion of the Diamond. *Scher. J.* 7, 362.
Allen & Pepys. Carbonic acid and Diamond. *N. Gehl*, 5, 664.
Theod. de Saussure. Combustion of Charcoal. *Ann. Chim.* 71, 254.
Guyton-Morveau. Combustion of the Diamond. *Ann. Chim.* 84, 20, and 233.
Sir Humphry Davy. Diamond, Graphite, and Charcoal. *Phil. Trans.* 1809, I., 69; *Schw.* 2, 42; also *Gilb.* 35, 433.
—————— Combustion of the Diamond and Charcoal. *Phil. Trans.* 1814, II., 557; *Schw.* 12, 200; also *Gilb.* 49, 1.
Silliman. Fusion of Carbon. *Sill. Am. J.* 5, 361; also *Schw.* 39, 190. *Sill. Am. J.* 6, 341; also *Schw.* 39, 87. *Ann. Phil.* 22, 311 and 468. *Sill. Am. J.* 10, 119.
Berzelius. Atomic Weight of Carbon. *Pogg.* 47, 199; also *Ann. Pharm.* 30, 241.
Dumas & Stas. Diamond, Plumbago, Atomic Weight. *Ann. Chim. Phys.* 76, 1; also *Ann. Pharm.* 38, 141; also *J. pr. Chem.* 22, 300.
Erdmann & Marchand. Diamond, Plumbago, Atomic Weight. *J. pr. Chem.* 23, 159.
Liebig & Redtenbacher. Atomic Weight of Carbon. *Ann. Pharm.* 38....113.

Carbonic Oxide.

Desormes & Clement. Carbonic oxide. *Gilb.* 9, 409; also *Scher. J.* 7, 327; also *Crell. Ann.* 1801, 2, 318, 415, and 474.
Deiman, Pats Van Troostwyk & Lauwerenburgh. *Scher. J.* 9, 261; also *Crell. Ann.* 1802, 2, 26.
Th. Saussure. *Gilb.* 13, 138.
Fownes. Action of Oil of Vitriol upon Ferrocyanide of Potassium. *Phil. Mag. J.* 24, 21; also *Manual of Chemistry, 2nd Ed.* p. 24.

Carbonic Acid.

Black. *Medical and Philos. Comm., by a Society in Edinburgh.*
Bergman. *Opusc.* 1, 1.
Priestley. *Experiments and Observations on different Kinds of Air.* 1, 43.
Thilorier. *Ann. Chim. Phys.* 60, 427; also *Pogg.* 36, 141. Further; *Ann. Pharm.* 30, 122.

Carbone, Carbonium, Kohlenstoff.

History. The evolution of carbonic acid gas in the burning of lime and in fermentation was known to Paracelsus and Van Helmont; subse-

quently, the properties of this gas were investigated by Hales, Black, Priestley, and Bergman. Lavoisier showed that it is composed of oxygen and another substance, *Carbon*, which he himself first proved to be a distinct element. He likewise showed that this element exists in a state of purity in the diamond, the volatilization of which in the focus of a burning mirror had been observed by the Florentine academicians in 1694. Lavoisier's statement, that the diamond when burnt is converted into carbonic acid, was confirmed by Smithson, Tennant, Mackenzie, Allen & Pepys, Morveau, Saussure, Sir H. Davy, Dumas & Stas, Erdmann & Marchand, and others. Lassonne (*Crell. N. Entdeck*, 2, 144), Priestley (*Crell. Ann.* 1800, 2, 256), and Woodhouse (*Gilb.* 9, 90), discovered carbonic oxide gas. Priestley regarded the production of this combustible gas, in the perfect absence of water, as contradictory to the theory of Lavoisier: but, on the other hand, it was shown by Cruikshank, Morveau, Clement & Desormes, Fourcroy & Thénard (*Gilb.* 9, 99; also *Scher. J.* 7, 224), W. Henry, Dalton, and Gay-Lussac & Thénard, that this gas does not contain hydrogen, but consists wholly of carbon and oxygen,

Sources. Pure in the diamond; mixed with iron, earthy matters, hydrogen, &c., in graphite or plumbago and anthracite; in the form of carbonic acid; and finally, in all organic bodies. The *Diamond* is probably carbon which has been fused at a high temperature and crystallized by slow cooling: thus, Göbel (*Pogg.* 20, 539) is of opinion that it is carbon reduced from carbonate of lime by some of the earth-metals at high temperatures. According to another view, diamond is carbon separated from decomposing organic compounds. Perfectly pure diamond would probably burn without residue; impure diamond leaves at least 0·05, and at most 0·2 per cent. of ash, sometimes in the form of a reddish-yellow powder, sometimes in straw-yellow crystalline particles. (Dumas & Stas.) Transparent diamonds leave scarcely any ash; those which are more or less opaque leave from 0·08 to 0·15 per cent. of reddish ash. (Erdmann & Marchand.) This ash, when examined by the microscope, appears to consist of laminæ and spiculæ, intermixed with a few roundish granules, some of the particles being black, opaque, and possessed of very strong lustre; some, brown-black and translucent; others yellowish-brown, yellow, or white, and transparent. They mostly exhibit a peculiar structure, sometimes that of dark-brown network, like vegetable parenchyma. The ash contains silica and iron. (Petzholdt, *J. pr. Chem.* 23, 475.) Nearly all diamonds when examined by the microscope, exhibit coloured portions in the form of roundish patches or clouds, in which no trace of organic structure can be discerned. In green diamonds, the deep emerald green parts become brown and black by ignition; but the colour of brown diamonds is not altered by the same treatment. (Wöhler, *Ann. Pharm.* 41, 346.)

Graphite from Wunsiedel yields only 0·33 per cent. of ash, consisting of potassa, silica, and oxide of iron: it is therefore nearly pure carbon. (Fuchs.) Graphite from Germany, specific gravity=2·273, contains 95·12 per cent. of carbon, and 5·73 per cent. of ash, chiefly consisting of grains of quartz. (Regnault, *Ann. Chim. Phys.* 66, 337.) Graphite from Bustletown, contains 95·4 per cent. of carbon, 0·6 of water, and 4·0 of silica, alumina, and the oxides of iron and manganese. (Vanuxen, *Sill. Am. J.* 10, 102.) The purest graphite from Ceylon yields only 1·2 per cent. of ash; other varieties 6 per cent., consisting of oxide of iron

and earthy matters. Graphite from the Himalaya mountains contains only 71·6, and English graphite only 53·4 per cent. of carbon, together with iron and large quantities of silica and alumina. (Prinsep, *N. Ed. Phil. J.* 13, 346.) According to Morveau, Davy, and Gay-Lussac & Thénard, graphite contains a small quantity of hydrogen; according to Allen & Pepys and Saussure, it contains none of that element. *Anthracite* closely resembles charcoal from organic bodies, and contains essentially —besides carbon and ash—from 1·5 to 4 per cent. of hydrogen, generally associated with oxygen and nitrogen in smaller quantity.

Preparation. 1. *Artificial Graphite.* (*a.*) Crude cast-iron as it flows from the blast-furnace, highly charged with carbon, deposits, on solidifying, a portion of the dissolved carbon in metallic-shining laminæ of graphite. (*b.*) Graphite in a similar state is obtained when a mixture of 2 parts of iron filings, 1 part of black oxide of manganese, and 1 part of lamp black, is heated to whiteness in a crucible. (Döbereiner, *Schw.* 16, 97.) To purify both the graphite of the blast-furnaces (*a*) and likewise native graphite, from iron and earthy matters, Dumas & Stas ignite the substance in the state of powder in contact with hydrate of potassa—wash the ignited mass with water—exhaust it with boiling aqua regia—then, after washing and drying the residue, subject it at a white heat for 18 hours to a current of dry chlorine gas: by this means, small quantities of chloride of iron and chloride of silicium, not removed by the aqua regia, are sublimed. In this state, the graphite is quite free from hydrogen, and when burnt, leaves either no residue or a mere trace of silica. Ceylon graphite, purified in this manner, was found by Erdmann & Marchand to yield, on burning, 0·5 per cent. of silica. Döbereiner purifies the graphite (*b*) by exhausting it with boiling aqua regia. According to Gay-Lussac (*Ann. Chim. Phys.* 4, 69), graphite thus purified still contains iron. The silica contained in graphite may likewise be removed by means of hydrofluoric acid. (Schaphäutl, *J. pr. Chem.* 19, 139.) When cast-iron, intersected with laminæ of graphite, is dissolved in aqua regia, the graphite remains behind mixed with gelatinous silica; and when the latter is removed by solution in caustic potassa and repeated boiling with water, there remains a kind of graphite, which when burnt leaves 2·6 per cent. of white ash. When cast-iron of this description is melted in a crucible, the iron runs off from the graphite, and the laminæ of that substance may be separated from iron still adhering to them, by reducing them to powder, and removing the iron by a magnet: in this manner, without the use of acid, the iron may be almost wholly removed. It appears then that iron is not, as was formerly supposed, an essential constituent of graphite. (Sefström, *Pogg.* 16, 168.) Karsten examined a specimen of graphite from a blast-furnace, of specific gravity 2·3285, and found it to burn without residue. A specimen examined by Wollaston contained manganese; one examined by the author left, on being burnt, a white residue, which exhibited the properties of silica.

2. *Charcoal.* This form of carbon is obtained by strongly igniting in a covered vessel such non-azotized organic compounds as, on burning, leave no fixed residue; *e. g.* pure sugar—or by passing the vapours of volatile organic compounds, such as alcohol, ether, volatile or fat oils, through white-hot porcelain tubes. Charcoal from sugar, even after being heated to whiteness, still contains 0·6 per cent. of hydrogen, and 3·1 per cent. of oxygen; and after further ignition for three hours in the

strongest blast-furnace, there yet remains 0·2 per cent. of hydrogen, and 0·5 per cent. of oxygen.

Under certain circumstances, a kind of carbon, free from hydrogen, and similar to graphite, appears to separate from organic compounds. 1. In porcelain-furnaces, which have not a good draught, carbon free from hydrogen is deposited in long, thin, dark-grey, non-crystalline threads, some straight, and some ramified, and exhibiting metallic lustre when examined by the microscope. (Gay-Lussac, *Ann. Chem. Phys.* 4, 67.) 2. *Gas-coke.* When coals are heated to redness in cast-iron gas-retorts, a quantity of carbon, free from iron and hydrogen, is deposited upon the upper parts and in the necks of the retorts, forming a hard, slaty substance of an iron-grey colour; also on cracks in the retorts, in the form of a warty mass, exhibiting a concentric and radiating structure. (Colquhoun.) In the preparation of steel by Makintosh's process, coal-gas is passed over red-hot iron bars contained in earthen vessels: if the gas is supplied so rapidly that the iron cannot take up the whole of its carbon, the excess of carbon is deposited in one of the three following forms: *a.* In metallic-shining, hard, dense masses of conchoidal fracture, scarcely to be scratched with a penknife. *b.* As a fine powder, similar to lamp-black, but heavier and of coarser grain. These two kinds cover the steel, and upon them is deposited: *c.* Carbon, in black, metallic-shining, capillary, and somewhat brittle threads, thousands of which are united like locks of hair: they are not combustible in the flame of a candle, but perfectly so in the blow-pipe flame. (Colquhoun, *Ann. Phil.* 28, 1; also *Kastn. Arch.* 9, 87; also *Br. Arch.* 23, 10; Braylay, *Ann. Phil.* 28, 192; also *Br. Arch.* 23, 15.) When oil-gas is passed over white-hot iron wire contained in a porcelain tube, the iron is converted into steel, and becomes coated with brittle graphite, containing 2 per cent. of iron; but at the same time there is deposited in the tube an elastic, brittle kind of graphite, which burns slowly, but without residue. (Sefström.)

Cagniard de la Tour's *Artificial Diamond* is charcoal, intimately mixed with a hard, crystalline slag, containing alumina and sesqui-oxide of iron, together with silica and sesqui-oxide of manganese. (Thénard, *J. Chim. Med.* 5, 38 and 39, also *Pogg.* 14, 525.) (Gannal's so-called *Artificial Diamond, J. Chim. Med.* 4, 382; also *Pogg.* 14, 387; 15, 311.)

Properties. The *Diamond* crystallizes in regular octohedrons and their modifications (*fig.* 2, 6, 8, and others); it is generally colourless and transparent, of extreme hardness, peculiar lustre, very high refracting power, and is a non-conductor of electricity. Native *Graphite, Plumbago,* or *Black Lead,* crystallizes in hexagonal tables of specific gravity 2·14 according to Fuchs, and 2·273 according to Regnault: it is steel-grey, soft, greasy to the touch, leaving a mark when rubbed on other bodies, and is a very good conductor of electricity. Artificial graphite possesses similar properties. *Charcoal* obtained by the ignition of organic substances, as well as that produced from the decomposition of carbonic acid, is an amorphous substance, of specific gravity about 1·57, opaque, black, often possessed of metallic lustre, soft (but becoming, after intense ignition, hard enough to scratch glass), and a very good conductor of electricity. Carbon in all its forms is one of the most difficult of all bodies to fuse or volatilize; it is also destitute of taste and smell.

The great difference between diamond, on the one hand, and graphite, or charcoal, on the other, is commonly attributed, partly to the different

degrees of purity of the carbon in these several forms, partly to differences in the state of aggregation of its atoms. The former of these explanations can only apply, in a certain degree, to charcoal, inasmuch as that substance generally retains small quantities of hydrogen and oxygen; but diamond and perfectly pure graphite consist wholly of carbon. The second explanation must therefore be resorted to in aid of the first. According to the latter, carbon in diamond belongs to the regular crystalline system; in graphite to the rhombohedral system; in charcoal it is amorphous. Fuchs (*J. pr. Chem.* 7, 353) regards graphite as amorphous, like charcoal, and supposes that the crystals of native graphite are pseudo-morphous crystals, formed from those of mica or sulphide of molybdenum. At all events, graphite and charcoal are much more nearly allied than diamond and graphite: the specific gravity of graphite is, however, greater than that of charcoal, and the crystallization of artificial graphite appears to be established beyond doubt. Still, however, it is extremely difficult to understand how dimorphism and amorphism should give rise to these marked diversities in the characters of a substance. In no other body are such decided differences produced by the same causes. Carbon in the diamond is transparent and a non-conductor of electricity, like the other non-metallic elements; but in graphite and charcoal it is opaque, possessed of metallic lustre, and a good conductor of electricity—and consequently approaches nearer to the metals: hence Döbereiner designated graphite as a metal, *Carbonium*.

A diamond placed on a support of lime or plumbago, and exposed to the flame of a powerful oxy-hydrogen blow-pipe, burns quickly away. The unconsumed portion is found to be rounded at the corners, and roughened on the surface; it has also lost much of its lustre, and exhibits numerous cracks, corresponding to the planes of cleavage. Whether superficial fusion takes place under these circumstances, is a point not yet decided. When graphite is heated in the oxy-hydrogen flame, a portion burns away, and a great number of fused globules are obtained, which are non-conductors of electricity, hard enough to scratch glass; some black, and affected by the magnet; others colourless, transparent, and non-magnetic. Anthracite yields similar transparent globules. (Silliman.) Diamond exposed on magnesia to the oxy-hydrogen blow-pipe, turns black, and splits into pieces exhibiting conchoidal fracture; when heated on pipe-clay, it exhibits numerous incisions, and appears to undergo partial fusion. (Murray, *Ann. Phil.* 22, 469.) When a diamond is heated in the oxy-hydrogen flame till the greater part is burnt away, the remaining portion is found to have its angles melted off, and appears half fused. (Marx, *Schw.* 47, 324.)

¶ The diamond, when exposed to a very high temperature produced by a Bunsen's battery of 100 plates, or by a condensed mixture of carbonic oxide and oxygen gas, fuses, and is converted into a mass resembling coke; its specific gravity is thereby reduced from 3·336 to 2·678. (Jacquelin, *N. Ann. Chim. Phys.* 20, 459.) ¶

On attaching to the polar wires of a deflagrator (I., 409) a couple of flexible leaden tubes—inserting into these tubes two cylinders of mahogany-charcoal, well boiled in water, from 1½ to 3 inches long, ½ an inch thick, and pointed in front—bringing these cylinders in contact, whereby they are brought to a state of vivid incandescence, and then separating the points by a short distance, they continue to glow vividly, form between them a bright luminous arc of flame, and send up a white smoke having a peculiar odour, like that of an electrical machine in strong action. On

the charcoal point of the zinc pole (from which the negative electricity issues) there is deposited—while the cylinder decreases on its sides—a quantity of additional matter, which grows to the length of half an inch, then breaks off, and is replaced by a new growth: on the contrary, the charcoal of the positive pole, from which the positive electricity issues, soon loses its point, and a cup-like cavity is formed in it, whilst at the same time it suffers but little diminution on the sides. To whichever part of the positive charcoal the point of the negative piece is directed, there the excavation is produced. If the two pieces of charcoal come in contact, they stick together. If the positive charcoal be replaced by a piece of metal, the negative piece receives no increase, but is gradually shortened during the combustion. In nitrogen gas, the two pieces of charcoal exhibit as brilliant a light, and the same growth of the negative point, as in air. Hence it appears that carbon, in the state of vapour, is transferred from the positive to the negative pole. If the eyes are protected by a pair of green spectacles, small particles of carbon may even be seen passing along the luminous arc from the copper pole to the zinc pole. The matter which accumulates on the negative point sometimes forms a cylinder, sometimes a round knob with a stem. When examined by a magnifying-glass, it exhibits a fused, warty or botremous, smooth, metallic-shining, greyish-black surface, and a non-fibrous structure; sinks rapidly in oil of vitriol; does not conduct electricity (hence its presence makes the charcoal less brightly incandescent—but on the removal of the fused portion, the brightness is restored); burns very slowly at a red heat, without visible flame, producing carbonic acid, and leaving, sometimes a yellowish-grey ash, sometimes none at all. It is not attacked by oil of vitriol, and very little by hot nitric acid. No sign of fusion ever appears on the positive charcoal. (Hare, Silliman.) The same result was obtained by Griscom (*Ann. Phil.* 22, 73), and even with an ordinary voltaic battery. (West, *Ann. Phil.* 21, 314.) When cylinders of maple-wood-charcoal, well boiled in hydrochloric acid and water and then strongly ignited, are subjected to the action of a powerful deflagrator, they instantly melt at their points to a vitreous mass, and likewise exhibit a depression on the copper and a cylindrical growth on the zinc side. Moreover, the copper charcoal always diminishes in weight: the zinc charcoal sometimes increases, especially when the experiment is made in a glass tube; sometimes remains of constant weight, and sometimes diminishes, though much less than the charcoal connected with the copper pole. (Silliman.)

If a cylinder of graphite an inch long, $\frac{1}{8}$ of an inch thick, and pointed at the end, is attached to the copper pole, and a piece of wood-charcoal to the zinc pole, the graphite becomes partly red hot; and on the edge of the ignited point, where also an emission of sparks takes place, globules of fused graphite are continually formed: in the space between the two points, which is filled with vapour of carbon, no sparkling takes place. At the point of the graphite, a black shining hollow is produced. On the other hand, the charcoal at the zinc pole becomes elongated, from the deposition of a fused mass, not in globules, but of a fibrous structure. Besides this, there are likewise globules formed upon it; and when the two points are placed in a vertical line, the graphite being uppermost, no globules are formed upon the latter, but a proportionally greater number (mostly black ones) on the charcoal point below. Similar effects are produced when the charcoal is connected with the copper, and the graphite with the zinc pole; or again, when graphite or charcoal is placed upon

both poles. When the graphite is connected with the zinc pole, it either retains it weight unaltered, or increases in weight, by covering itself with fused carbon, as much as the charcoal connected with the copper pole diminishes. The globules on the charcoal are shining, rarely black, more frequently brown, yellow, greyish-white, or sometimes quite colourless, and at the same time either slightly cloudy or quite transparent. Most of them, when examined by the microscope, appear to be quite free from any admixture of charcoal. The graphite globules are almost always black (never colourless). They scratch glass, and are non-conductors of electricity. The coloured ones only are slightly attracted by the magnet (because they contain iron). They are extremely difficult to burn: when ignited with chlorate of potassa, they yield large quantities of carbonic acid. They constitute, therefore, a form of carbon closely allied to the diamond. (Silliman.) The globules, when burnt in the oxy-hydrogen flame, leave but very little residue: when strongly heated with nitre they detonate, and form carbonate of potassa, with which there is mixed a small quantity of peroxide of iron. Hence they consist of carbon, with a very small quantity of iron. (Hare, *Sill. Am. J.* 10, 110.)

According to Vanuxen (*Schw.* 43, 253; *Sill. Am. J.* 10, 102), on the contrary, these globules are nothing but the fused ashes of the charcoal and graphite, and consist mainly of iron and silica. Vanuxen likewise showed that graphite, anthracite, and mahogany-charcoal, when heated by the oxy-hydrogen blow-pipe, yield a greater number of globules, both of the colourless and non-magnetic, and the black and magnetic variety, in proportion as they contain more ash; whereas lamp-black, pressed together into the form of a cylinder, and containing only $\frac{1}{100}$ of its weight of ash, yields no globules. On the other hand, Hare has defended his opinion in the *Philosophical Magazine*, 65, 283; and in *Silliman's Journal*, 10, 110, he maintains that the oxy-hydrogen blow-pipe is not adapted for the fusion of carbon, inasmuch as the oxygen burns the carbon, and leaves nothing but the fused ash. It is greatly to be regretted that Hare and Silliman, in their experiments, did not select a kind of charcoal which does not leave any ash.

Atomic weight of Carbon: 6, according to Dumas & Stas, Erdmann & Marchand; 6,06832, according to Liebig & Redtenbacher; 6·13, according to Berzelius.

Compounds of Carbon.

Carbon and Oxygen.

The affinity of carbon for oxygen is one of the most powerful in existence.

A. Carbonic Oxide. CO.

Carbonic acid gas, Gaseous Oxide of carbon, Carbonous acid gas; incorrectly: *Oxidated Carburetted Hydrogen gas, Gas hydrogène oxycarburé.*

Found, together with carbonic acid gas, in the intestinal canal of *hooved* cattle. (Pflüger, *Kastn. Arch.* 9, 98.)

Formation. 1. When bodies which retain oxygen with a certain degree of force are ignited with charcoal or plumbago.—When vapour of water is passed over well-burnt charcoal kept at a red heat in a por-

celain tube, (*App.* 9.), decomposition takes place, and hydrogen, carbonic oxide, and carbonic acid gas are produced (Clement & Desormes, *Gilb.* 9, 423). 100 volumes of the gaseous mixture thus obtained contain 56·21 hydrogen gas, 28·96 carbonic oxide, 14·63 carbonic acid, and 0·19 marsh gas; therefore exactly 2 atoms of carbonic oxide to 1 atom of carbonic acid: this, however, is perhaps accidental. When common charcoal not previously ignited is used, the gaseous mixture contains 7·55 measures of marsh-gas, which is likewise evolved when the charcoal is ignited alone (Bunsen, *Pogg.* 46, 207)*. When a large quantity of vapour of water acts upon a small quantity of charcoal, the hydrogen gas produced is *accompanied* chiefly by carbonic acid gas, with but a small quantity of carbonic oxide. (Gm.)†—All metallic oxides which give up their oxygen to charcoal at a strong red heat, as oxide of zinc, black oxide of iron, and protoxide of manganese, convert the carbon, either into carbonic oxide, or a mixture of that gas with carbonic acid.—The gas evolved from iron furnaces contains from 25 to 32, that from copper-refining furnaces 13 to 19 per cent. of carbonic oxide. (Bunsen, *Pogg.* 46, 193; 50, 81.)

2. Carbonic oxide is likewise formed when carbonic acid, either free or combined with an alkali, comes in contact with charcoal or iron at a red heat, and gives up to these substances its second atom of oxygen, which is less intimately combined than the first. (*Scheme* 14.)

3. In the dry distillation of many organic compounds.

4. In the decomposition of oxalic or formic acid by oil of vitriol.

5. In the decomposition of ferrocyanide of potassium by oil of vitriol.

Preparation. 1. In a gun-barrel fitted with a glass tube (*App.* 37), oxide of iron, zinc, lead, or copper, is heated to redness with ignited charcoal or plumbago; or carbonate of potassa, soda, baryta, strontia, or lime, with ignited charcoal, plumbago, or iron filings;—or carbonic acid gas is passed repeatedly over iron filings or previously ignited charcoal kept at a red heat in a gun-barrel.—The carbonic acid largely mixed with the gas thus obtained is removed by agitation with milk of lime or solution of potassa.

2. Oxalic acid, or an oxalate or formiate is heated with oil of vitriol, and the carbonic acid removed as above.—Döbereiner heats oxalic acid with oil of vitriol, and removes the carbonic acid by lime or potassa.—Dumas (*Ann. Chim. Phys.* 33, 110) heats binoxalate of potassa with 6 parts of oil of vitriol, and passes the mixture through aqueous solution

* Bunsen says, that an opinion has hitherto been universally entertained, and has also found its way into treatises on chemistry, that marsh-gas is produced in the action of aqueous vapour on ignited charcoal. Nevertheless, the reaction was correctly given by Clement & Desormes 41 years ago. In the 2nd and 3rd editions of *Gmelin's Handbuch*, also, nothing is said of the production of marsh-gas in this manner.

† We often meet with the erroneous assertion that the heat which may be obtained by the combustion of charcoal is increased by the addition of water. Those who make this assertion forget that when the oxygen entered into combination with the hydrogen to form water, a certain quantity of heat was developed which must be deducted, now that the water is decomposed by the carbon. The quantity of heat evolved is the same, whether carbonic acid is formed from the combination of carbon and oxygen, or carbonic acid and water from carbon, oxygen, and water,—excepting that in the latter case an additional quantity of heat is rendered latent in the formation of vapour of water. The access of water lessens the *glow-fire*, but produces a greater quantity of flame, in consequence of the formation of carbonic oxide and hydrogen gases.

of potassa.—Mitchell (*Sill. Am. J.* 25. 344) heats crystallized oxalate of ammonia with from $\frac{1}{8}$ to $\frac{1}{4}$ of its weight of oil of vitriol: by this means, pure carbonic oxide free from carbonic acid, is evolved from the beginning to the end of the process. According to Gale (*Phil. Mag. J.* 6, 232), on the contrary, this method yields carbonic oxide gas mixed with an equal volume of carbonic acid.

¶ 3. Finely-powdered yellow ferrocyanide of potassium, heated with eight or ten times its weight of oil of vitriol, yields carbonic oxide in a state of perfect purity.—One atom of crystallized ferrocyanide of potassium and 6 atoms of oil of vitriol produce 6 atoms of carbonic oxide, 2 atoms of sulphate of potassa, 3 atoms of sulphate of ammonia, and one atom of protosulphate of iron (Fownes). ¶

Properties. Colourless gas. [For its refracting power and specific gravity, *vid.* pp. 95 and 279, Vol. I.]—It is inflammable; does not support the combustion of other bodies; has no taste, but a faint peculiar odour; small animals immersed in it die instantly. When inspired, it produces giddiness and fainting fits (Clement & Desormes), even when mixed with a fourth of its bulk of air (H. Davy); it is much more poisonous than carbonic acid.

				Vol.	Sp. gr.
C	6	42·86	Vapour of carbon?	1·0	0·4160
O	8	57·14	Oxygen gas	0·5	0·5546
CO	14	100.00	Carbonic oxide gas	1·0	0·9706

(CO = 76·44 + 100 = 176·44. Berzelius.)

Decompositions. Heated potassium or sodium decomposes this gas, the former taking fire in it—the products being oxide of potassium or sodium and charcoal (Gay-Lussac & Thénard *Recherches*, 1, 266).—Under certain circumstances, potassium seems to absorb carbonic oxide gas without decomposing it (*vid. Croconic acid*).—Carbonic oxide is likewise decomposed by the passage of electric sparks through it, or by being passed through a red-hot tube.

Combinations. Water absorbs $\frac{1}{80}$ of its volume of this gas, according to Davy; $\frac{1}{27}$, according to Dalton; and $\frac{1}{16}$ according to Saussure.

Carbonic oxide gas likewise combines with chlorine.

B. Carbonic Acid. CO^2.

Acid of air, Luft-säure (Bergman), *Acid of chalk, Kreidesäure* (Keir), *Acide carbonique, Acide méphitique* (G. Morveau) *Kohlensäure*; in the gaseous state: *Carbonic acid gas, Fixed air* (Black), *Mephitic air, kohlensäures Gas, Gas acide carbonique, Gas carbonicum, Gas sylvestre, Spiritus sylvestris.*

Sources. Carbonic acid issues in the form of gas from the ground in various localities (Grotta del Cane, Pyrmont, Brohl; in the last mentioned place, according to G. Bischof (*Schw.* 56, 129), the quantity discharged in 24 hours amounts to 600 lbs.). Carbonic acid is present in the air in the ratio of 0·0005 of its volume; more abundantly in cellars and mines (*Choke-damp*),—in all waters, but principally in acid and chalybeate waters; in combination with ammonia, potassa, soda, baryta, strontia, lime, magnesia, protoxide of manganese, oxide of zinc, and the protoxides of lead, iron, and copper; finally, in certain organic liquids.

Formation. 1. In the combustion of carbonaceous substances in air or in oxygen gas:—*a.* Diamond takes fire in oxygen gas at a strong red heat (more easily than graphite, according to Dumas & Stas) and burns with a brilliant red light, and great development of heat, sufficient, according to Sir H. Davy, to fuse platinum: it is almost wholly consumed, even when the supply of heat from without is cut off: the unburnt residue is white and opaque. According to Guyton-Morveau, blackening takes place at an earlier stage of the combustion.—*b.* Plumbago likewise requires a very high temperature, burns very slowly, and like diamond, ceases to burn in the open air as soon as the supply of heat from without is interrupted.—*c.* Organic substances, especially charcoal, require but a dull red heat to cause them to enter into combustion; and the process once begun generally proceeds spontaneously in the air. The combustion of charcoal in oxygen gas is brilliant and attended with rapid emission of sparks. In many chemical processes which take place in organic bodies, carbon combines either with oxygen contained in the body itself, or with that of the air, the combination taking place, sometimes at ordinary, sometimes at slightly elevated temperatures, and the product being carbonic acid: *e. g.* in Fermentation, Putrefaction, and Respiration. In the combustion of diamond and pure graphite, the volume of the gas remains unaltered, the oxygen consumed being replaced by an equal volume of carbonic acid gas. Charcoal burns with a slight diminution of the volume of gas, in proportion to the hydrogen which it contains; but when the proper deduction is made for the water produced, the quantity of carbonic acid generated is found to be not less than that produced by the combustion of diamond. According to Von Wrede's experiment (I., 258, *at top*), the volume of carbonic acid gas produced under the ordinary atmospheric pressure must be somewhat less than that of the oxygen consumed; but under a pressure of half an atmosphere, the volumes of the two gases must be exactly equal.

2. When carbonaceous bodies are brought in contact, either at ordinary or at higher temperatures, with many of the less intimate compounds of oxygen.—Thus, carbonic acid is formed when charcoal is boiled in sulphuric acid, nitric acid, &c., or when charcoal, diamond, or graphite is ignited with vapour of water, with nitrates, chlorates, or iodates, or with red oxide of mercury, black oxide of manganese, and various other metallic oxides.

3. In the combustion of carbonic oxide. Two volumes of carbonic oxide gas combine with one volume of oxygen to form 2 volumes of carbonic acid gas. (Gay-Lussac.) The combination is induced by a red heat, by the electric spark, platinum, &c., and is sometimes slow, sometimes rapid. When the two gases are mixed, it is accompanied by a slight detonation, and the production of a bluish flame: when the combustion takes place gradually, the gas exhibits a pale blue, lambent flame, but if previously heated to redness, a yellow flame.

Carbonic oxide gas is inflamed even by the heat of a red-hot coal, or red-hot iron. (H. Davy.) The carbonic oxide must amount to at least $\frac{1}{7}$, and the oxygen to at least $\frac{1}{15}$ of the whole, to enable the mixture to take fire by the electric spark. A mixture of carbonic oxide and air continues to burn on the surface of a heated spiral of platinum wire. (H. Davy.) Ordinary platinum foil does not act on a mixture of carbonic oxide and oxygen below 300°. (Dulong & Thénard.)—Platinum foil prepared according to Faraday's method (p. 47), condenses, in three days, half a cubic inch of a mixture of 2 cubic inches of carbonic oxide and 1 cubic

inch of oxygen. The carbonic acid gas produced retards the action; consequently, the condensation takes place more quickly when the gaseous mixture is placed over solution of potassa, which takes up the carbonic acid as fast as it is formed. (W. Ch. Henry.) Spongy platinum introduced into a mixture of 2 volumes of carbonic oxide and 1 volume of oxygen gas induces slow combustion; but, according to Döbereiner and W. Henry, not till the temperature is raised; according to the latter, at 150°: according to Dulong & Thénard, and W. Ch. Henry, on the contrary, it acts at ordinary temperatures. According to the latter, the spongy metal acts more quickly than the prepared foil, and with particular rapidity when potassa is present, in which case ⅔ of the gaseous mixture are condensed in two hours. Platinum-paper-ash (p. 50) acts at ordinary temperatures: to make it red-hot in the gaseous mixture it must be heated to 30°, according to Pleischl, and to 80° according to De la Rive & Marcet. Liebig's platinum-black instantly becomes red-hot in a mixture of carbonic oxide and oxygen, and sets fire to the mixture: even in pure carbonic oxide gas it becomes red-hot, and produces carbonic acid, because it already contains oxygen absorbed within its pores. (W. Henry, W. Ch. Henry.) Palladium-paper-ash acts upon the gaseous mixture at ordinary temperatures, and becomes red-hot when heated to 120°. (Pleischl, De la Rive & Marcet.) Carbonic oxide is also ignited by iridium-black, but not by spongy iridium. (Döbereiner.) Gold-leaf does not act below 300°. (Dulong & Thénard.) If spongy platinum be allowed to act at 171° on a mixture of 2 measures of hydrogen, 2 of carbonic oxide, and 1 of oxygen, till condensation no longer takes place, it is found that the quantity of oxygen which has combined with the hydrogen is to that which has combined with the carbonic oxide and formed carbonic acid, as 1 : 4 : if such a mixture is heated in a glass tube without spongy platinum till the glass softens, slow combustion takes place, and the ratio is as 3 : 2 ; thirdly, when such a mixture is inflamed by the electric spark, the ratio of the quantities of oxygen which combine with the hydrogen and with the carbonic oxide, is as 3 : 1. Hence it appears that, at higher temperatures, the oxygen combines by preference with the hydrogen; at lower temperatures, with the carbonic oxide. (W. Henry.)

Preparation. 1. *In the liquid state: a.* On the small scale, according to Faraday's method (I., 286). The oil of vitriol must be made to act very slowly on the carbonate of ammonia; otherwise the tube will burst, in consequence of the great heat evolved. (Niemann.)—*b.* On the large scale. In a cast-iron cylinder, 49 centimetres long, and 27 wide, containing about 6 litres, having walls 5 centimetres thick, strengthened by 6 ribs, and provided in the middle with pins on which it rests in an upright position, and can be moved to and fro for the purpose of mixing the contents,—carbonic acid is evolved from 1800 grammes of bicarbonate of soda, 4 litres of water at 35°, and 1000 grammes of oil of vitriol*. When the decomposition is quite complete, the carbonic acid is made to pass through a tube furnished with a stop-cock, into a similar cylinder placed horizontally, in which the greater part of the acid collects and condenses, the first cylinder becoming heated by the action of the acid on the water and the carbonate of soda. After a minute, the cocks are closed, the cylinders separated, and the charge in the first renewed; and this process is repeated a third time, so that the horizontal cylinder receives

* 2¾lbs. of bicarbonate of soda, 6½lbs. of water, and 1½lb. of oil of vitriol.

at least three charges, and becomes filled for the greater part with liquid carbonic acid. After seven charges, the quantity of carbonic acid obtained amounts to 4 litres. (Thilorier, *Ann. Pharm.* 30, 122.) O. Hervey was killed by the bursting of the first cylinder, while swinging it to and fro for the purpose of mixing the second charge. (*J. Chim. Med.* 17, 61.) Mitchel proceeds in the same manner as Thilorier. Brunel (*J. Pharm.* 12, 301) recommends compression of the gas by means of a pump.

2. *In the solid state.* From the second cylinder of Thilorier's apparatus, the carbonic acid is made to pass through a tube into a perforated cylindrical brass box divided into two equal parts by a partition. If the stopcock be closed after the lapse of five seconds, a snow-like mass of solid carbonic acid about as large as a duck's egg is found in the box. (Thilorier.) When an ounce of liquid carbonic acid is suffered to escape in the gaseous form by opening the vessel, a dram of solid carbonic acid remains behind, having the appearance of magnesia alba. (Mitchell.)

3. *In the gaseous state.* Cold dilute sulphuric or hydrochloric acid is poured upon chalk contained in a gas-generating vessel (*App.* 41). The acid combines with the lime, and sets the carbonic acid free. (*Scheme* 12.) To free the gas from liquid mechanically carried over, it may be passed through water contained in the vessel *b* (*App.* 43). Mohr (*Ann. Pharm.* 29, 268) places pieces of chalk on a plate of glass or copper *c* (*App.* 44), suspended by a wire in the lower part of a glass bottle *b*, the bottom of which has been removed—immerses this bottle in a vessel filled with dilute hydrochloric acid—and fits the upper opening of the bottle with stopper, cock, and gas-delivery tube *e*. As often as gas is let out at the top, acid enters the bottle, and coming in contact with the pieces of chalk, evolves fresh gas. The gas is received over water or mercury. In cases in which the presence of nitrogen is not hurtful, carbonic acid gas may be prepared by passing a stream of air over red-hot charcoal.

Properties. Solid carbonic acid presents the appearance of a white, floculent mass resembling snow, and compressible like that substance. A spirit thermometer immersed in it sinks to —87° (—124·6° F); if the whole column of alcohol were immersed in the mass, the temperature indicated would be —93° (—135·4° F). When exposed to the air, the acid disappears in a few minutes, and often leaves behind it a small quantity of water condensed from the air by the cold. Touched with the finger when resting on a smooth surface, it glides quickly forward, as if supported by a stratum of gas. The freezing point of carbonic acid is situated at —65° (—85° F). A piece of solid carbonic acid pressed upon the skin of an animal, stops the circulation at the point of contact by the depression of temperature which it produces, forms a white spot, and after fifteen seconds a blister: if the carbonic acid be then removed, a white depression with raised edges is produced; then suppuration takes place, and finally, the wound heals and leaves a scar. Hence it appears that cold produces effects similar to those of heat, attended, however, with less pain. (Mitchell, *Ann. Pharm.* 37, 354.)

Liquid carbonic acid is transparent and colourless, and has a refracting power much smaller than that of water. (H. Davy & Faraday.) According to Niemann (*Br. Arch.* 36, 190), it is extremely mobile, and refracts light almost as strongly as water. Its specific gravity at —20° is 0·90; at 0°, 0·83; at + 30°, 0·60°. (Thilorier.)

[For the expansion of liquid carbonic acid by heat, see I., 225; vaporization of carbonic acid and cold produced thereby, I., 259, 271, 273,

and 275; elasticity of the vapour at the state of maximum tension, I., 261.] Carbonic acid gas standing over liquid carbonic acid in a close vessel contains at 0°, $\frac{1}{13}$ of its volume, and at 30°, $\frac{1}{3}$ of its volume of liquid carbonic acid, the volume of the latter being estimated at 0°. (Thilorier.) Liquid carbonic acid obtained by the action of sulphuric acid upon carbonate of ammonia, exhibits a higher tension, in proportion as the sulphuric acid is less diluted with water; probably because the admixture of water with the carbonic acid raises its boiling point. Thus, at 12·5°, the tension of the carbonic acid amounts to 58 atmospheres, when it has been prepared with sulphuric acid of specific gravity 1·840; to 50 atmospheres, with acid of 1·7; to 49, with acid of 1·5; to 46 with acid of 1·3; and to 44 atmospheres, with acid of 1·1 specific gravity. (Niemann, *Ann. Pharm.* 1, 35.)

At ordinary pressures, carbonic acid is a colourless gas. (For its refracting power and specific gravity, see I., 95 and 279.) It is incombustible, and does not support the combustion of most other bodies. The slight reddening which it imparts to tincture of litmus disappears on exposure to the air, in consequence of the evaporation of the acid. It produces turbidity in baryta, strontia, and lime-water, when passed through them. It has a slightly irritating odour; and when inhaled, either pure or mixed with a tolerable quantity of air, it produces asphyxia and death.

Calculation.			Dumas & Stas.	Lavoisier.	Clem. & Desormes.	Th. Saussure.	Tennant.	Allen & Pepys.
C	6	27·27	27·27	24 28	27 29	27·04 ....27·38	28	28·6
2O	16	72·73	72·73	76 72	73 71	72·96 ....72·62	72	71·4
CO^2	22	100·00	100·00	100 .. 100	100 .. 100	100 .. 100	100	100·0

	Vol.	Sp. Gr.	or	Vol.	Sp. Gr.
Carbon vapour?	1	0·4160	Carbonic oxide gas	1·0	0·9706
Oxygen gas	1	1·1092	Oxygen gas.....................	0·5	0·5546
Carbonic acid gas	1	1·5252	Carbonic acid gas	1·0	1·5252

($CO^2 = 76{\cdot}44 + 2 \,.\, 100 = 276{\cdot}44$. Berzelius.)

Decompositions. By the continued passage of electric sparks, carbonic acid gas is resolved into carbonic oxide and free oxygen. (W. Henry, Dalton.) The quantity of the gas thus decomposed must always be small, since the electric spark causes the oxygen and carbonic oxide to recombine. The liquid acid is not decomposed in the voltaic circuit. (Niemann.)

2. Into carbonic oxide and combined oxygen, by the passage of electric sparks, when hydrogen gas, mercury, or other metals are likewise present (Saussure, *Gilb.* 13, 129 and 134); also when heated to redness in contact with hydrogen gas, charcoal, iron, or zinc (p. 89).

3. The whole of the oxygen is withdrawn, and carbon separated by heated potassium or sodium (*Sch.* 21), the former becoming red hot, and both being converted into alkaline carbonates. (H. Davy, Gay-Lussac & Thénard.) A similar effect is produced by phosphorus (*Sch.* 20; Smithson Tennant, *Crell. Ann.* 1793, 1, 158), and by boron (Gay-Lussac & Thénard), when these substances come in contact at a red heat with carbonic acid in combination with a fixed alkali (see I., 124). Liquid carbonic acid is decomposed by potassium with effervescence, even in the cold, but not by zinc, lead, iron, or copper (Thilorier); phosphorus does not decompose it, even when heated. (Niemann.)

Combinations. *a.* With water.—The liquid acid does not mix with water, but floats on the top after being shaken up with it. (Thilorier, Mitchell.) *Aqueous carbonic acid.* Water, at ordinary temperatures, absorbs its own volume of carbonic acid gas, and thereby requires a specific gravity of 1·0018; at increased pressure and lower temperatures it takes twice or three times as much, estimating the quantity by weight: *Acid Water, Sauerwasser.*—Water impregnated with carbonic acid has a sharp and slightly acid taste. Heat, the action of the air-pump, exposure to the air, or congelation, causes the carbonic acid to escape (compare page 68).

b. Carbonic acid unites with most salifiable bases, forming salts called *Carbonates.* In its affinity for bases, it is one of the weakest of all acids; and in consequence of the feebleness of its acid properties, it does not mask the alkalinity of ammonia, potassa, and soda, when united with them in simple atomic proportions (page 7). From the same cause, it may be separated by heat from all bases excepting ammonia, potassa, soda, and lithia. The carbonates are likewise decomposed by most other acids, the carbonic acid escaping as gas with its own peculiar odour. All basic and normal carbonates are insoluble in water, excepting those of ammonia, potassa, soda, and lithia; but all acid carbonates are soluble in water, to a certain extent, indeed, existing only through its agency. The soluble carbonates, as well as free carbonic acid, may therefore be detected in solution by the white precipitate soluble in hydrochloric acid, which they give with lime, strontia, or baryta-water. Baryta-water is rendered slightly turbid by a solution of carbonate of soda containing 1 part of carbonic acid in between 40,000 and 80,000 parts of water; to produce a sensible precipitate in lime-water, the proportion of water must not exceed 20,000 parts to 1 part of carbonic acid. (Lassonne. *J. Chim. Med.* 8, 523.)

¶ The following table of the solubility of certain earthy and metallic carbonates in water saturated with carbonic acid is given by Lassaigne (*J. Chim. Med.* 1848, June, p. 312.) ¶

							In Equivalents.
Carbonate of lime	....	at	0°	in	1428	pts. water	.... $6CO^2$: 1CaO
——	—	at	10°	in	1136	——	.... ,, ,,
——	baryta	at	10°	in	588	——	.... $6CO^2$: 1BaO
——	strontia	at	10°	in	838	——	.... $6CO^2$: 1SrO
——	manganese ..	at	—	in	2000	——	.... $3CO^2$; MnO
——	silver	at	10°	in	961		
——	zinc				1428		
——	copper				3333		
——	lead				7144		

c. Carbonic acid gas is absorbed by alcohol and other organic liquids.*

Other Compounds of Carbon.

A. With Phosphorus.—B. With Sulphur.—C. With many metals, especially Iron, forming *Metallic Carbides or Carburets.*—D. In all organic compounds.

* The compounds of carbon and hydrogen will be described among organic compounds.

Chapter IV.

BORON.

Homberg. Boracic Acid. *Crell. Chem. Archiv.* 2, 265.
Geoffroy. Boracic Acid. *Crell. n. Chem. Archiv.* 3, 217.
Gay-Lussac & Thénard. Decomposition of Boracic Acid. *Recherches.* 1, 276; also Gilb. 30, 363.
Sir H. Davy. Decomposition of Boracic Acid. *Phil. Trans.* 1809, I., 75; *Schw.* 2, 48; *Gilb.* 35, 440.
Berzelius. Boracic Acid. *Schw.* 23, 160.—Boron and Boracic Acid. Pogg. 2, 113.—Boracic Acid. *Pogg.* 34, 560.
L. Gmelin. Boracic Acid. *Schw.* 15, 245.
Soubeiran. Boracic Acid. *J. Pharm.* 11, 29 and 558; also *N. Tr.* 11, 1, 191; also *Mag. Pharm.* 11, 13.
Tünnermann. Boracic Acid. *Kastn. Arch.* 20, 1.

Boracium, Bora, Bor, Bore.

History. Homberg, in 1702, discovered boracic acid in borax. In 1808, this acid was decomposed by Gay-Lussac & Thénard, and immediately afterwards by Sir H. Davy, into oxygen and the previously unknown element, *Boron.*

Sources. Boron, together with iodine, bromine, and selenium is among the least abundant of the non-metallic elements: it occurs exclusively in the form of boracic acid.

Preparation. Vitrefied boracic acid in the state of powder, mixed with an equal weight of potassium cut up into small pieces, is heated to redness for some minutes in a tube of iron, copper, platinum, or glass, connected with a pneumatic tube. The mass is then well boiled with very dilute hydrochloric acid, washed with water, and dried at a gentle heat. (Gay-Lussac & Thénard.) Boracic acid being seldom perfectly anhydrous, the process is generally attended with detonation and spirting. In proportion as the potassa-salt is removed by washing, the boron becomes mixed with the water in so very fine a state of division, that it runs through the filter; and, when the greater part of the salt has been removed, even dissolves in the water to a slight extent, imparting a yellow colour to it. The addition of acids or salts to the water prevents the fine division and solution of the boron. It is better, therefore, to wash with water containing sal-ammoniac, and then remove the sal-ammoniac by means of alcohol. Boron thus obtained is tolerably free from silicium. (Berzelius.) If the boracic acid be deprived *as much as possible of water* by fusing it in a platinum crucible, and then *coarsely* pounded—and a double quantity of potassium be used, freed from the crust of hydrate of potassa, &c., which generally adheres to it,—the mixture, when gradually heated in a glass tube over a spirit-lamp, and kept at a red heat for ten minutes, produces no explosion, but undergoes tranquil decomposition,—and after being boiled with water acidulated with hydrochloric acid (which causes no evolution of hydrogen gas), and then washed on a filter

with pure water, it yields boron. (R. D. Thomson, *Phil. Mag. J.* 10, 419.)

2. Gaseous fluoride of boron is passed—first through a tube filled with crystallized boracic acid—then through another containing peroxide of lead, to free it from fluoride of silicium and sulphurous acid—and lastly over heated potassium, which, as soon as the black crust formed at the commencement has burst, burns with a red flame and produces a mixture of boron and fluoride of potassium. The latter is removed by washing with water, which however is attended with considerable difficulty. Boron thus obtained contains 0·4 of silicium, which remains behind when the boron is dissolved in nitric acid; moreover, the solution has a yellow colour, proceeding from carbon previously mixed with the potassium. (Berzelius.)

3. Fluoride of boron and potassium, dried by a heat almost amounting to redness and then pounded, is placed, together with an equal quantity of potassium, in a tube of iron or glass closed at the bottom (from the latter, however, a portion of silicium may be reduced). Heat is then applied till the potassium melts, and the mass is worked about with a steel wire till a uniform mixture is obtained; it is then heated to redness, at which temperature the fluorine is transferred, without detonation, from the boron to the potassium. The mass is next freed, by repeated boiling in water containing sal-ammoniac, from fluoride of potassium and from the undecomposed and very difficultly soluble fluoride of boron and potassium (the greater the excess of potassium used, the smaller is the quantity of this latter compound which remains: in the decomposition of fluoride of boron and sodium by metallic sodium, no such difficultly soluble salt would be formed). The boron is then ignited in an atmosphere of hydrogen, whereby it evolves water and hydrofluate of boracic acid, and loses its capability of diffusing itself through water and dissolving in it. Finally, it is washed repeatedly with water and dried in vacuo. Boron thus obtained is tolerably pure, but when burned in oxygen, produces small quantities of water and carbonic acid. (Berzelius.)

4. Hydrated chloride of boron is decomposed at a red heat by hydrogen gas. (Dumas, *Ann. Chim. Phys.* 31, 376.)

Döbereiner's method (*Schw.* 16, 116) of preparing carbonized boron by placing a mixture of 109·5 parts of ignited borax with 11·4 of lamp-black in a gun-barrel and heating it to whiteness for two hours,—then exhausting the fused mass with boiling water, and finally with hydrochloric acid—did not prove successful, either in Pleischl's hands or in the author's.

Properties.—Dark greenish brown, opaque, friable, not capable of scratching glass. After exposure to a white heat out of contact of air, it sinks rapidly in oil of vitriol. It neither melts nor sublimes even at the strongest white heat; does not conduct electricity. Tasteless and inodorous. (Gay-Lussac & Thénard.)

Compounds of Boron.

Boron and Water.

Aqueous Solution of Boron.—Freshly prepared, unignited boron dissolves in pure water, producing a greenish-yellow solution. Acids and salts separate the boron from the solution. When the liquid is evaporated

in a glass dish, a greenish-yellow film is produced on the edge, easily separable, and only partially soluble in fresh water. (Berzelius.)

Boron and Oxygen.

Boracic Acid. BO^3.

Sedative Salt, Narcotic Vitriol-Salt, Boronsäure, Borsäure, Acide boracique, Acide borique, Acidum boracis, Sal sedativum Hombergii, Sal narcoticum vitrioli.—Found in the free state in solution in the *Laguni* of Tuscany—small hot lakes, into which vapours rise from the volcanic bottom: the boracic acid crystallizes on the edges of these lakes in the form of *Sassolin.* It also occurs in combination with salifiable bases in Tincal, Boracite, Hydroboracite, Datolite, and Botryolite, and in small quantities in Schorl, Apyrite, Axinite, and Rhodizite.

Formation.—Of all the non-metallic elements, boron and carbon have the strongest affinity for oxygen. Boron does not oxidize in the air or in oxygen gas at ordinary temperatures—but oxidation begins at about 300°. It then burns in the air with a reddish light, but in oxygen gas with dazzling brightness, and always with lively emission of sparks (according to Berzelius, a green flame is likewise observed). Boracic acid sublimes, and there remains a black substance* covered with glassy boracic acid: this substance, by alternate washing and combustion several times repeated, may likewise be converted into boracic acid. (Gay-Lussac & Thénard.)

Boron does not decompose water at a boiling heat: it readily decomposes oil of vitriol when heated, and nitric acid, even though but slightly concentrated, in the cold—the product in all cases being boracic acid. At a red heat, it decomposes—sometimes with development of light and heat, and in the case of nitre, with brisk detonation—carbonic, sulphurous, sulphuric, nitrous and nitric acids combined with alkalis, an alkaline borate being formed, while carbon, sulphur or nitrogen is set free. It also decomposes many of the heavy metallic oxides at a red heat; and if the oxide is in excess, the part of it which remains undecomposed unites with the boracic acid produced and forms a borate. (Guy-Lussac & Thénard.) Hydrate of potassa heated with boron is converted, with evolution of hydrogen gas, into borate of potassa. From an aqueous solution of chloride of gold, boron precipitates metallic gold. (Berzelius.)

Preparation. 1. The water of the Laguni, evaporated in leaden pans by the heat of the vapours which issue from the grounds, yields the *Tuscan Boracic acid,* as it is prepared on the large scale (Bowring, *N. Ed. Phil. J.* 28, 85; also *Ann. Pharm,* 34, 350;—Payen, *Ann. Chim. Phys.* 76. 247;—Thomson *Repert.* 68, 382).—The acid thus obtained contains 3. 18 per cent. of ammonia. (Erdmann, *J. pr. Chem.* 13, 72.) It contains only 76. 494 per cent. of crystallized boracic acid, besides 8·5 sulphate of ammonia, and smaller quantities of free sulphuric acid, the sulphates of potassa, soda, lime, magnesia, protoxide of manganese, sesqui-

* This substance is distinguished from ordinary boron by its black colour, and by the higher temperature which it requires for combustion. Gay-Lussac & Thénard do not decide whether it contains oxygen or not: according to Davy, it is a suboxide of boron, containing 0·25 oxygen: according to Berzelius, it is boron, merely mechanically altered by elevation of temperature.

oxide of iron, and alumina,—also sal-ammoniac and silica. (Wittstein, *Repert.* 72, 145.)

2. A solution of one part of borax in 4 parts of boiling water is mixed with one-third the quantity of oil of vitriol: on cooling, the boracic acid crystallizes out: an additional quantity may be obtained by further evaporating and cooling the liquid. The liquid may also be evaporated to dryness and the boracic acid extracted by hot alcohol. (Meissner, *N. Tr.* 1, 2, 460.)—Wackenroder (*N. Br. Arch.* 21, 313) uses hydrochloric acid in preference to sulphuric, because the latter adheres more obstinately to the separated boracic acid. Formerly, the acid was prepared by sublimation: *e. g.* by heating to redness in a retort a mixture of 16 parts borax, 2 water, and 5 oil of vitriol. The powdered residue was repeatedly moistened with water and again ignited. The product was much smaller than that obtained by the process above described.

To purify the crystallized acid from adhering sulphate of soda, it is again dissolved in hot water and re-crystallized: afterwards, it is fused in a Hessian or platinum crucible till the liquid mass becomes tranquil—by which treatment it is freed from water, sulphuric acid, and the oily matter which adheres to the borax—then poured out, and the *Vitrefied Boracic acid* preserved in well stopped bottles. *According to Robiquet (Ann. Chim. Phys.* 17, 216), *it still, when in this state, retains* 0·225 *of water, of which it can only be deprived by ignition with oxide of copper.*

Properties. Boracic acid forms a colourless, transparent, very hard, very coherent, and brittle glass; specific gravity, at 4° (39·2°F.) in vacuo = 1·83. (Royer & Dumas.)—It fuses at a red heat, but is perfectly fixed in the fire when alone; whereas when united with water, aqueous acids, or alcohol, it partly vaporizes in company with them. Boracic acid fused in a platinum crucible cracks spontaneously on cooling and exhibits, along the cracks, a vivid light visible even by day. (Dumas, *Ann. Chim. Phys.* 32, 335; also *Pogg.* 7, 535.) It is perfectly inodorous; destitute of corrosive power; has a slightly bitter but not sour taste (E. Davy, *N. Ed. Phil. J.* 6, 131); and reddens litmus but very feebly. Its alcoholic solution and its mixture with sulphur (*Taschenb.* 1780, 88) burn with a green flame.

	Calculation.		Berzelius.	Davy.		Gay-Lussac & Thén. (approx.)
B	10·8	31·04	31·1896	33	36	67
3O	24	68·96	68·8104	67	64	33
BO^3	34·8	100·00	100·0000	100	100	100

(BO^3 = 136·2 + 3 . 100 = 436·2 . Berzelius.)

Berzelius formerly estimated the atomic weight of boron at double its present value, and supposed that in boracic acid 6 atoms of oxygen were united with one of boron. The atomic weight of boracic acid was thereby made twice as great as it is reckoned in the preceding table, according to the latter hypothesis of Berzelius, viz. 21·6 + 6. 8 = 69·6. According to the new hypothesis, the borates contain twice as many atoms of acid as they were supposed to contain according to the old. Assuming the truth of the new theory, the atomic weight of boracic acid (that of hydrogen = 1) is, according to the experiments of Payen (*J. Chim. Med.* 4. 159) = 35·14; of Berzelius = 34·8; of Soubeiran = 32·8.

Decompositions. Potassium, at elevated temperatures, decomposes boracic acid with evolution of light and heat; sodium effects the decom-

position quietly. (Gay-Lussac & Thénard.)—Charcoal does not decompose it at a white heat; neither does phosphorus when its vapour is made to pass over red-hot borate of baryta. (Gm.) The decomposition which Sir Humphry Davy thought he observed in the voltaic circuit, appears, from the experiments of Faraday and Connell, to be rather doubtful.

Combinations.—*a.* With water.

α. Hydrate of Boracic acid.—Obtained by heating the crystallized acid considerably above 100°; it then loses half its water. (Berzelius.)

	Calculation.		Berzelius.
$2BO^3$	69·6	72·05	71·88
$3HO$	27	27·95	28.12
$3HO, 2BO^3$	96·6	100·00	100·00

β. Crystallized Boracic acid. This compound crystallizes on cooling from a hot solution, in white scaly six-sided laminæ, having a faint pearly lustre, flexible, and greasy to the touch: when the solution is contaminated with sulphuric acid or fatty matters, the crystals acquire a much larger size than when they separate from a pure solution. Crystalline system, the doubly oblique prismatic (*Fig.* 129). $y : v = 80° 30'$, $y : u = 84° 53'$, $y : z = 75° 30'$, $v : u = 118° 30'$, $v : z = 120° 45'$, $u : z = 120° 45'$ (this must be a misprint in the memoir); perfectly cleavable parallel to y: frequently, macle-crystals, in which the axis of rotation is parallel to the line of intersection of u and v, and the surface of junction parallel the face z. (Miller, *Pogg.* 23, 558.)—Sp. gr. = 1·479. (Kirwan.)

	Calculation.		Davy.	Payen.	Berz.	Pleischl.		Thomson.
BO^3	34·8	56·31	57	56·66	56	56	55	55·5
$3HO$	27	43·69	43	43·34	44	44	45	44·5
$3HO, BO^3$	61·8	100·00	100	100·00	100	100	100	100·0

The crystals retain their water at 100°, but give up half of it, without melting, at a higher temperature, and the whole of it with great frothing at a red heat, the aqueous vapour carrying with it a portion of the hydrated boracic acid.

γ. Aqueous solution of Boracic acid. One part of the crystallized acid dissolves in 25·66 parts of water at 19°, in 14·88 at 25°, in 12·66 at 37°, in 10·16 at 50°, in 6·12 at 62·5°, in 4·73 at 75°, in 3·55 at 87·5° and in 2·97 parts at 100° (Brandes & Firnhaber, *Br. Arch.* 7, 50).—The specific gravity of a solution saturated at 8° is 1·014. (Anthon.) When the solution is evaporated, a large quantity of boracic acid is volatilized.

b. With salifiable bases, boracic acid forms a class of salts called *Borates.* Its affinity for bases is but little greater than that of carbonic acid; but at a red heat it expels all acids which are more volatile than itself. In the borates, one atom of base is united with $\frac{2}{3}$, 1, $1\frac{1}{3}$, $1\frac{1}{2}$, 2, 3, 4, or 6 atoms of acid. Most of these salts may be melted into a transparent glass, which dissolves various metallic oxides with characteristic colours: they are not decomposed at a red heat by charcoal or phosphorus. Most acids separate the boracic acid from them; consequently, when they are heated in contact with sulphuric acid and alcohol, the alcohol burns with a green flame. If a red-hot platinum wire be dipped into a pounded mixture of any borate with an equal quantity of bisulphate of potassa, and then held in the blowpipe flame, the flame will

exhibit a green tint. (Turner, Erdmann, *Schw.* 59, 86.) All the borates, with the exception of those of ammonia, potassa, soda, and lithia, are difficultly soluble in water.

c. Boracic acid dissolves in several of the stronger acids, especially in sulphuric acid.

d. It is soluble in alcohol and oils.

Boron and Hydrogen.

Boruretted Hydrogen-gas? Boron heated in hydrogen gas does not dissolve in it. The gas evolved by the action of boride of potassium upon water is supposed by Davy to be boruretted hydrogen gas. By heating to whiteness a mixture of iron filings and $\frac{1}{10}$ of vitrefied boracic acid, the author obtained a coherent mass which he supposed to contain a small quantity of boride of iron, together with boracic acid and metallic iron. On dissolving this substance in hot hydrochloric acid, a gas was obtained which smelt like the hydrogen gas evolved from water by the action of cast iron. This gas, when mixed with air, burned with strong detonation and a reddish-yellow flame; exhibited, when slowly burned, a yellow flame with a green border; formed a white cloud with nitrous acid; but did not absorb a greater quantity of oxygen than pure hydrogen absorbs. The author attributed these peculiarities to the presence of a small quantity of boron; but they are more probably due to the other impurities usually present in hydrogen gas evolved by the aid of iron. (*Vid.* p. 44.)

Other Compounds of Boron. With Sulphur, Sulphuric acid? Chlorine, Hydrochloric acid? Fluorine, and Potassium.

Chapter V

PHOSPHORUS.

Phosphorus in General.

Kunckel, in his *Laboratorium Chymicum*, Hamb. and Leipz. 1716, p. 660.
Boyle. *Philosophical Transactions.* No. 135, 196, and 198.
Homberg. *Mém. de l'Acad. des Sc.* 1692. p. 101.
Marggraf, in *seinen Chemischen Schriften.* Berl. 1762, B. 1. s. 42.
Crell. *Crell. Chem. J.* 1, 23; 2, 137; 4, 88.
Thénard. *Ann. Chim.* 81, 109; also *Schw.* 4, 212; also *Gilb.* 44, 341. *Ann. Chim.* 85, 326; also *Gilb.* 46, 270.
H. Davy. *Phil. Trans.* 1809, I, 67. *Schw.* 1, 481; also *Gilb.* 35, 288. *Schw.* 1, 484; also *Gilb.* 36, 184. *Phil. Trans.* 1812, 405; also *Schw.* 7, 494; also *Gilb.* 46, 273. *Phil. Trans.* 1818, 316; also *Ann. Phil.* 13, 210; also *Schw.* 30, 294; also *N. Tr.* 3, 2, 405.

Gay-Lussac & Thénard. Verification of the Decomposition Experiments of Davy, &c. *Recherches*, 1, 187; also *Schw.* 1, 488; also *Gilb.* 35, 292.

Phillips. Behaviour of Phosphorus in Water. *Ann. Phil.* 21, 470.

White Phosphorus and Red Phosphoric Oxide.

Böckmann. *Ueber das Verhalten des Phosphors in mehreren Gasarten.* Erl. 1800. Action of Light upon Phosphorus. *Scher. J.* 5, 243.

A. Vogel. Action of Light upon Phosphorus. *Schw.* 7, 95; also *Gilb.* 45, 63. *Gilb.* 48, 375.

Pelouze. *J. Chim. Med.* 8, 530; also *J. Pharm.* 18, 417; also *Schw.* 65, 444; also *Ann. Pharm.* 3, 52.

H. Rose. White Phosphorus.

Leverrier. *Ann. Chim. Phys.* 65, 257; also *Ann. Pharm.* 27, 167; also *J. pr. Chem.* 14, 18.

Hypophosphorous and Phosphorous Acid.

Fourcroy & Vauquelin. Salts of Phosphorous acid. *J. Polytechn.* 4, 655.

Thomson. Phosphorous acid. *Ann. Phil.* 15, 227; also *N. Tr.* 5, 2, 441.

Dulong. Hypophosphorous and Phosphorous acids. *Ann. Chim. Phys.* 2, 141; also *Schw.* 18, 164.

H. Rose. Hypophosphorous acid. *Pogg.* 9, 225, and 361; 12, 77, and 288.—Phosphorous acid. *Pogg.* 8, 205; 9, 23, and 215.

Wurtz. Acids of Phosphorus. *Ann. Pharm.* 58, 49.

Phosphoric Acid.

Wiegler. Phosphoric acid from Bones. *Crell. N. Entd.* 2, 5.

Val. Rose. Composition of Phosphoric acid. *N. Gehl,* 2, 309.

Thomson. *Ann. Phil.* 7, 305; also *Schw.* 17, 222.

Dalton. *Manchester, Mem. Sec. Ser.* 3; *abstr. Ann. Phil.* 15, 136.

Berzelius. Composition of Phosphoric and Phosphorous acids and their salts. *Gilb.* 53, 393; 54, 31; also *Ann. Chim. Phys.* 2, 151. 217, and 329. Further: *Ann. Chim. Phys.* 10, 278.

Mitscherlich. Salts of Phosphoric acid. *Ann. Chim. Phys.* 19, 350.

Gay-Lussac. Modifications of Phosphoric acid. *Ann Chim. Phys.* 41, 331; also *N. Tr.* 20, 1, 261.

Clark. *Ed. J. of Sc.* 7, 298; also *Schw.* 57, 421; also *N. Tr.* 20, 1, 243.

Stromeyer. *Schw.* 58, 123.

Graham. *Pogg,* 32. 33. *Ann. Pharm.* 29, 19.

Gregory. Preparation of Phosphoric acid from Bone-ash. *Ann. Pharm.* 54, 94.

Maddrell. On the preparation of Phosphoric acid, and on the Metaphosphates. *Mem. Chem. Soc.* 3, 273; *Ann. Pharm.* 61, 53.

Fownes. Existence of Phosphoric Acid in Rocks of Igneous Origin. *Phil. Trans.* 1844; abstr. *Ann. Pharm.* 60, 190.

Sullivan. On the same subject. *Phil. Mag. J.* 27, 161; abstr. *Ann. Pharm.* 60, 190.

Rammelsberg. Phosphates. *Pogg.* 64, 251, and 405; abstr. *Ann. Pharm.* 56, 210.

Fleitmann & Henneberg. Phosphates. *Ann. Pharm.* 65, 30—Double Pyrophosphates. *Ann. Pharm.* 65, 387.
Schwartzenberg. Pyrophosphates. *Ann. Pharm.* 65, 133.
Persoz. Double Pyrophosphates. *Ann. Pharm.* 65, 163.
Baer. On certain Phosphates and Pyrophosphates. *Pogg.* 75, 152; abstr. *Ann. Pharm.* 68, 255.

Phosphuretted Hydrogen.

Gengembre. *Crell. Ann.* 1789, 1, 450.
Kirwan. *In. s. Phys. Chem. Schriften,* 3, 96.
Raymond. *Scher. J.* 5, 389.
Berthollet. *Scher. J.* 5, 396.
Thomson. *Ann. Phil.* 8, 87; also *Schw.* 18, 357. Further: *Ann. Phil.* 15, 227; 16, 262; 17, 10; 18, 120; 24, 203, and 247.
Dalton. *Ann. Phil.* 11, 7; also *Schw.* 24, 325.
Houton Labillardière. *Ann. Chim. Phys.* 6, 304; also *Schw.* 21, 100.
Vauquelin. *Ann. Chim. Phys.* 25, 401.
Dumas. *Ann. Chim. Phys.* 31, 113; also *N. Tr.* 13, 1, 145.
H. Rose. *Pogg.* 6, 199; 8, 191; 14, 183; 24, 109, and 295; 32, 467; 46, 633.
Buff. *Schw.* 57, 449; also *Pogg.* 16, 363.
Graham. *Phil. Mag. J.* 5, 401; also *J. pr. Chem.* 3, 400; abstr. *Ann. Pharm.* 13, 141.
Leverrier. *Ann. Chim. Phys.* 60, 174; also *Ann. Pharm.* 18, 333.
Paul Thénard. *N. Ann. Chim. Phys.* 14, 5; *Ann. Pharm.* 55, 27; abstr. *Ann. Pharm.* 52, 238.

Metallic Phosphides.

Pelletier. *Crell. Ann.* 1796, 2, 148.
Grotthuss. *Ann. Chim.* 64, 19; also *N. Gehl,* 5, 599.
H. Rose. *Pogg.* 24, 318.
Landgrebe. *Schw.* 53, 460; 55, 96.
Berthier. *Ann. Chim. Phys.* 33, 180.

Kunckel's Phosphorus, Brandt's Phosphorus, Phosphor, Phosphore, Phosphorus Urinæ.

History. Brandt, of Hamburg, accidentally discovered phosphorus in 1669; Marggraf in 1740 demonstrated the individuality of phosphoric acid, which had been regarded by Scheele as phlogisticated muriatic acid. Gahn, in 1769, pointed out the existence of this acid in bones; and Scheele devised a process for extracting it. Lavoisier first proved the separate existence of phosphorous acid, which had been previously noticed by Sage; Pelletier gave a process for obtaining it by the slow combustion of phosphorus; Fourcroy & Vauquelin examined the compounds of the acid thus formed; Dulong, however, showed that it is a mixture of phosphorus and phosphoric acid,—and that pure phosphorous acid in the hydrated state can only be obtained by the method devised by Davy. Dulong likewise discovered hypophosphorous acid. Lavoisier, Val. Rose, Thénard, Berzelius, Dulong, Thomson, Davy, and H. Rose determined the composition of the acids of phosphorus. The isomeric modifications of phosphoric acid,

viz., the pyrophosphoric and metaphosphoric acids, were examined by Gay-Lussac, Clark, Stromeyer, and more particularly by Graham. Pelouze showed that the red substance formerly examined by Böckmann, Thénard, and A. Vogel, is really an oxide of phosphorus. Gengembre in 1783, and Kirwan in 1784 discovered phosphuretted hydrogen gas, which Davy in 1812 obtained in a less inflammable state: this modification of the gas was afterwards more minutely examined by H. Rose. Pelletier examined a great many metallic phosphides.

Sources. Phosphorus occurs in tolerably large quantity, almost always in the form of phosphoric acid, in combination with various bases, in all the three kingdoms, but especially the animal; rarely as phosphuretted hydrogen; also in the meteoric iron of Bohumiliz, Buenos Ayres, and Gotha.—Also in various rocks of igneous origin. (Fownes; Sullivan.)

Preparation. A mixture of charcoal with phosphoric acid containing lime, or of charcoal and phosphate of lead, is placed in an earthen retort—a number of which are generally arranged side by side in a reverberatory furnace (*Galeeren-ofen*)—and distilled at a heat gradually rising to whiteness. The carbon then deprives the phosphoric acid of its oxygen—is itself thereby converted into carbonic oxide which escapes as gas—and sets the phosphorus at liberty. (*Sch.* 83.)—The neck of the retort is usually connected with a copper tube bent knee-shape, and having its further extremity immersed to the depth of a line in water contained in a two-necked receiver. The phosphorus condenses below the surface of the water, while the carbonic oxide gas passes off through the second opening of the receiver, which is provided with an escape-tube directed upwards. The carbonic oxide gas is mixed with vapour of phosphorus, and likewise with phosphuretted hydrogen, the quantity of which is greater as the mixture of charcoal and phosphoric acid contains a larger proportion of water. Pure phosphoric acid is not so well adapted to the purpose as that which contains lime,—according to Javal (*Ann. Chim. Phys.* 14, 207), because it partly volatilizes undecomposed,—according to Graham (*Lehrb.* 2, 172,) because it cannot be so completely deprived of water, and therefore yields a greater quantity of phosphuretted hydrogen.

1. From human urine, inasmuch as this liquid contains phosphate of ammonia and phosphate of soda; *a.* The urine, evaporated to the consistence of honey, is distilled, either by itself, or mixed with sand or charcoal powder. (Brandt; Boyle.) In this process, the carbon—either that which is produced by the decomposition of the organic matter in the urine, or that which is added to it—decomposes only that portion of phosphoric acid which is in combination with ammonia, not that which is combined with soda.—*b.* Marggraf mixes the urine, evaporated to the consistence of honey, with 0·1 chloride of lead and 0·5 charcoal powder, and heats the mass till it becomes pulverulent, then distils it. The chloride of lead and phosphate of soda yield, by double decomposition, chloride of sodium and phosphate of lead.—*c.* Giobert mixes the urine, not evaporated, with nitrate (or acetate) of lead; the precipitate, which consists of phosphate, sulphate and chloride of lead, he washes thoroughly; mixes it with a fourth of its weight of charcoal powder; dries the mixture in a pan; and then distils.

2. From burnt bones, which consist for the most part of phosphate of lime; *a.* By preparing calcareous phosphoric acid; mixing it, after con-

centration to the consistence of a syrup, with one-third of its weight of charcoal powder; drying the mixture, and distilling.—α. 100 parts of bone-ash are digested for a considerable time in a leaden vessel with 90 parts of oil of vitriol and 950 of water: the solution filtered through linen, evaporated to a syrup, mixed with 20 parts of charcoal powder, and dried, yields 10 parts of phosphorus. (Funcke, *Br. Arch.* 3, 204.)—β. A mixture of 3 parts bone-ash, 2 parts oil of vitriol, and 16 parts water, is similarly treated, and, after being concentrated to a syrup, mixed with $\frac{3}{4}$ parts charcoal to a doughy consistence. The mixture is then heated to redness, with constant stirring, in an iron vessel, and when cool, put into the retort as quickly as possible. (Graham.)—γ. Nicolas uses equal weights of bone-ash and oil of vitriol —δ. Scheele dissolves the bone-ash in nitric acid, precipitates the lime by sulphuric acid, filters, concentrates, &c.—*b*. By preparing phosphate of lead, and distilling it with $\frac{1}{8}$ of its weight of charcoal ; α. Fourcroy & Vauquelin prepare acid phosphate of lime by Nicolas's method, and precipitate its aqueous solution with acetate of lead.—β. Berzelius dissolves the bone-ash in warm nitric acid, and mixes it while still hot with acetate of lead. Native phosphate of lead may also be used, provided it is free from arseniate.

Two parts of bone-black mixed with one part of fine quartz-sand, and raised to a strong white heat in an earthenware tube, yield carbonic oxide and a small quantity of phosphorus. (Wöhler, *Pogg.* 17, 178.) The affinity of silicic acid for lime assists the decomposing action of the charcoal on the phosphoric acid combined with the lime.

The phosphorus which passes over is freed from adhering charcoal and red phosphoric oxide by pressing it between chamois-leather under warm water; or by distillation in a glass retort the neck of which dips under water. It is then melted in glass tubes and formed into sticks.*

The phosphorus of commerce frequently contains arsenic, as was first observed by Hertz & Bärwald. (*Berl. Jahrb.* 32, 2, 113.) For, if the oil of vitriol used in its preparation has been formed by the combustion of arsenical sulphur, it will contain arsenious acid; and when bone-ash is decomposed by it, the arsenious acid will mix with the phosphoric acid; consequently, when the mass is heated with charcoal, the arsenic will be reduced to the metallic state and will pass over with the phosphorus. In one sample of phosphorus, Wittstock found 0·76 per cent. of arsenic. (*Berl. Jahrb.* 32, 2, 125; abstr. *Pogg.* 31, 126.) Phosphorus of this description has the same tenacity and the same colour as pure phosphorus; but the surface, when freed from the white crust, is of a smoky yellow colour, while the inner portion exhibits the pale yellow tint of pure phosphorus. It cannot be purified by distillation, for the arsenic passes over with it. It is, like the latter, perfectly soluble in bisulphide of carbon, but the solution soon deposits a red sediment, consisting of bisulphide of carbon and phosphoric oxide. To water under which it is kept for some time, it imparts arsenious acid. (Wittstock.) If it be digested for half an hour

* An apparatus by which the last-mentioned part of the process may be performed on the large scale with great regularity and expedition, is described by Seubert, *Ann. Pharm.* 49, 346. It consists of a copper vessel in which the phosphorus is melted, and from which it flows into glass tubes placed horizontally, and having half their length—that towards the copper vessel—surrounded with warm water, the other half with cold. The phosphorus, as it solidifies in the cold part of the tubes, is drawn out; a fresh quantity flows from the receiver to supply its place; this, in its turn, is solidified and drawn out;—and thus a stick of phosphorus is formed of any required length. By this method from 15 to 20lbs. of phosphorus may be formed into sticks in a quarter of an hour. The memoir is accompanied by a figure of the apparatus. [W.]

with 2 parts of nitric acid of specific gravity 1·1, the acid takes up the greater part of the arsenic, which may then be easily recognised by means of sulphuretted hydrogen (Bärwald); but it is only when the phosphorus has been digested with continually renewed quantities of dilute nitric acid, till it is reduced to $\frac{1}{8}$ of its original bulk, that it can be considered perfectly free from arsenic. (Wittstock.) When the solution of this impure phosphorus in dilute nitric acid is evaporated, it becomes turbid at a certain degree of concentration, in consequence of the complete separation of the arsenic in the form of a black powder, its reduction being effected by the phosphorous acid present and the phosphuretted hydrogen evolved when it is heated. (Bärwald, Wittstock: *compare* Dalk, *Berl. Jahrb.* 34, 1, 247; Wackenroder, *J. pr. Chem.* 2, 340; Liebig, *Ann. Pharm.* 11, 260.)

A sample of phosphorus obtained from France was covered with a greyish-yellow coating instead of a white one; appeared, when freed from this coating, of a dark-red colour by transmitted light; was almost black on the fractured surface; and retained this colour when melted and slowly solidified. It contained, besides arsenic, bismuth, lead, iron, and copper—a particularly large quantity of antimony; and when dissolved in bisulphide of carbon, deposited black flakes of sulphide of antimony. (Wittstock, *Berl. Jahrb.* 33, 2, 146.)

Many specimens of phosphorus are yellow in the fused state, but turn black on cooling, especially when suddenly cooled. Boiling in alcohol destroys this property: on the other hand, phosphorus acquires it by being fused with phosphoric acid. (Bonz, *Crell. Ann.* 1788, 1, 392; Thénard.)

Phosphorus, otherwise pure, generally contains a small quantity of phosphoric oxide, which gives it a yellowish or reddish colour. (*Vid.* p. 108.) To free it from this oxide and obtain it colourless, the following methods may be applied:

1. By digesting it for a considerable time, with frequent agitation, in very dilute nitric acid contained in a flask fitted with a gas-delivery tube which dips under water. The phosphoric oxide is then converted into phosphorous and phosphoric acid more quickly than the phosphorus. Chlorine water acts in a similar manner.

2. By heating the phosphorus in a solution of potassa or ammonia, and then in water.

3. By heating it in a solution of hydrate of potassa in alcohol of 75 per cent., whereby it is, in a few minutes only, converted into a clear watery liquid. Phosphorus thus treated does not solidify under the solution of potassa for several weeks at ordinary temperatures; but at —2·5° it solidifies rapidly, and subsequently fuses at its ordinary melting point. If poured upon blotting-paper, it solidifies as soon as the adhering solution has sunk into the paper, and with particular rapidity when touched with an iron wire. On pouring off the solution of potassa and sprinkling the phosphorus with water as cold as can be procured, it instantly solidifies to a snow-white, easily crumbling mass of crystalline texture. When more slowly cooled by water, it solidifies to a white mass of waxy consistence. If this white phosphorus be strongly heated with solution of potassa, then freed from the liquid after the lapse of three minutes, and several times sprinkled with very cold water, it is obtained, sometimes perfectly transparent, sometimes only translucent. (R. Böttger, *Schw.* 67, 141.)

4. Ten parts of phosphorus are added to one part of bisulphide of carbon

placed below alcohol of 80 per cent.: the phosphorus dissolves, whilst the phosphoric oxide and the white crust rise to the surface of the solution. About 11 parts of solution of potassa are then added, and heat applied for about eight minutes, till the white and red substances are dissolved, and the bisulphide of carbon is converted into xanthonate of potassa. After cooling, the alkaline liquid is poured off—the phosphorus repeatedly washed with cold water—heated under alcohol containing a small quantity of potassa, till all the bisulphide of carbon is expelled (the presence of sulphide of carbon makes the phosphorus crumbly and even pappy), and washed with cold water. Phosphorus thus purified appears snow-white when suddenly cooled, but perfectly transparent after slow cooling.

Phosphorus should be kept in the dark in vessels filled with water.

To *granulate* phosphorus, it is shaken up, while in the fused state, with a warm liquid till it solidifies. For this purpose, according to Cassarca, (*J. Pharm.* 16, 202), alcohol of 36° B. is better adapted than water. According to Böttger (*Beiträge*, 1, 65; 2, 127), the liquid which reduces phosphorus to the finest state of granulation is human urine; and it derives this property from the urea which it contains, so that an aqueous solution of artificial urea may be used as a more cleanly substitute for the urine. A tall cylinder an inch wide is half filled with a liquid of this kind, and heat applied till the phosphorus introduced into it is melted: the phosphorus is then worked about for two minutes, by means of a twirling stick which passes through the opening of the wooden cover of the cylinder; it is thus brought into a fine state of division. The remaining portion of the cylinder is then filled with cold water, the twirling motion being continued all the while. When the liquid comes to rest, the phosphorus is deposited in the state of powder; the liquid is then poured off, and the phosphorus washed with water.

Properties. Phosphorus is colourless, transparent after slow cooling, semi-opaque after rapid cooling, and has a waxy lustre. It crystallizes in regular octohedrons and rhomboidal dodecahedrons. Considerable masses of phosphorus, when they solidify after fusion, yield dodecahedrons and octohedrons as large as peas. (Trautwein, Buchner, *Kastn. Arch.* 10, 127, and 504; *Repert.* 25, 481.) From a solution in volatile oils, phosphorus crystallizes in octohedrons (Pelletier); and from solution in sulphide of phosphorus, in dodecahedrons. (Mitscherlich.) Specific gravity = 1·896, *Böckmann*, 2·0332, *Fourcroy*, 2·089 at 17° (that which has been purified by an alcoholic solution of potash), *Böttger*. It is brittle in the cold, but of a waxy consistence at ordinary temperatures. At 34·33° it becomes brittle, and easy to pulverize; melts at 44·5 (J. Davy, *N. Ed. Phil. J.* 6, 130); after fusion it cools, if at rest, down to 37·5° before it solidifies; and when solidification takes place, the temperature rises to 45°. (Pelletier.) According to Heinrich, it fuses at 46·25°, and solidifies at 40°, its temperature then rising again to 46·25°. In the fused state it presents the appearance of a transparent oil. Melted phosphorus, when at rest, often remains liquid considerably below its melting point (I., 9 and II. 105); frequently even as low as 4°: under these circumstances, contact with a solid body, especially with phosphorus, causes it to solidify. (Bellani, *Giorn. di fisica*, 1813; also *N. Quart. J.* 2, 469; H. Rose, *Pogg.* 32, 469.) This phenomenon is particularly remarkable with phosphorus boiled in an aqueous or alcoholic solution of potassa, which remains liquid for days and then solidifies on being agitated. Grotthuss (*N. Gehl*, 9, 228) likewise, on heating phosphorus with alcoholic solution of potassa,

obtained it in the form of an oil which did not solidify on cooling, and when heated in contact with water, evolved phosphuretted hydrogen, without introducing phosphoric acid into the water: hence he concluded that the oil must be a compound of phosphorus and hydrogen.

Phosphorus boils at 250° (Heinrich), at 288° (Dalton), at 290° (Pelletier, *Ann. Chim.* 4, 3), and is converted into a colourless vapour. (Specific gravity of the vapour, p. 279, vol. I.) Phosphorus volatilises at temperatures considerably below its boiling point, not only when boiled with water, in which case it makes the aqueous vapour luminous, but in small quantities, even at ordinary temperatures, either in vacuo or in a space filled with air (I., 265, 266). Oxygen, hydrogen, carbonic oxide, hydrosulphuric acid, nitrogen, &c., and likewise carbonic acid gas, (according to Davy, but not according to Fourcroy & Vauquelin) when placed in contact with phosphorus, become charged with its vapour. The faint luminosity said to be observed when phosphorus volatilizes in nitrogen gas is due, according to Berthollet, to a trace of oxygen introduced through the water which confines the gas, and giving rise to a slow combustion. Berthollet asserts that nitrogen gas, by taking up vapour of phosphorus, increases in volume by $\frac{1}{40}$; but according to Brunner (*Ann. Chem. Phys.* 78, 316), no perceptible increase takes place, inasmuch as the quantity of phosphorus which volatilizes at ordinary temperatures is extremely small, not amounting to one milligramme in 1732 cubic centimetres.

Phosphorus, both in the solid and in the liquid state, is a non-conductor of electricity. According to Knox (*Phil. Mag. J.* 16, 188), melted phosphorus conducts the current of a 60-pair battery with plates 5 square inches in surface.

Phosphorus, when exposed to the air, smells like garlic; in the state of solution it has a sharp and repulsive taste, and acts as a violent irritant poison. It is highly inflammable.

White Phosphorus. Phosphorus, kept under water and exposed to sunshine or ordinary daylight, gradually becomes covered with an opaque crust, which is reddish-yellow at first but afterwards turns white, has a specific gravity 1·515 at 15° (Pelouze), smells like phosphorus, shines in the dark on exposure to the air, but turns red in daylight more quickly than colourless phosphorus. This white phosphorus retains its original appearance when dried over oil of vitriol; but at a temperature not amounting to 50°, it changes into transparent melted phosphorus, and that too without losing water or sustaining any diminution of weight. The white variety is therefore pure phosphorus, differing from the transparent kind only in its state of aggregation. (H. Rose, *Pogg.* 27, 563.) Marchand (*J. pr. Chem.* 20, 506) finds that white phosphorus dried over oil of vitriol loses by fusion only from 0·4 to 0·7 per cent. of water. Pelouze (*Ann. Chim. Phys.* 50, 83), who dried white phosphorus without oil of vitriol, found that when fused it lost 12 per cent. of water: he therefore regarded it as a *Hydrate of Phosphorus* = P^2, HO. Mulder (*J. Pharm.* 23, 20; also *J. pr. Chem.* 13, 383) regards it as a compound of phosphoric oxide and phosphuretted hydrogen, produced by decomposition of water—because it turns red in water containing air. This reddening was not observed by Marchand, not even when oxygen gas was passed through the water. Mulder's result was probably due to the action of light. The production of white phosphorus may perhaps be explained on the supposition that phosphorus, under the influence of light, decomposes water, producing phosphoric oxide and phosphuretted hydrogen, and that, in the dark, these two compounds are again resolved into

water and finely divided phosphorus. At all events, phosphorus retains its transparency when constantly kept under water in the dark. (Gm.)

¶ *Red Phosphorus. Amorphous Phosphorus.* This modification of phosphorus has been already noticed on page 105, the author there speaking of it as phosphoric oxide. It is produced when phosphorus is exposed to light, either under water or alcohol, or in vacuo (even the Torricellian vacuum), or in hydrogen, nitrogen, carbonic acid, carburetted hydrogen, or, in short, any gas not containing oxygen. For this reason it was regarded by Berzelius, not as phosphoric oxide, but as phosphorus in a peculiar *allotropic** condition; while those who consider it as an oxide attribute its formation, under the circumstances just mentioned, to the presence of moisture not completely removed from it previously to its introduction into the several gases. The subject has lately been more particularly investigated by Schrötter (*N. Ann. Chim. Phys.* 24, 406; abstr. *Ann. Pharm.* 68, 247), who has shown, in a variety of ways, that the red substance in question is nothing but pure phosphorus in a peculiar state of aggregation. Perfectly pure colourless phosphorus, dried as completely as possible, was placed in a glass tube having a bulb in the middle; dry carbonic acid gas passed over it; the phosphorus gradually heated to 100°, to drive off every trace of moisture; and the tube sealed at both ends: by this means every trace of oxygen was excluded. Nevertheless it was found that the phosphorus, when exposed to light, assumed a red colour, the depth of which increased with the intensity of the light. The colouring did not extend to the whole mass, but was due to the formation of a multitude of small, separate, red particles. The same results were obtained in hydrogen or nitrogen gas. It appears, then, that light produces in phosphorus a peculiar change of condition, which cannot be ascribed to oxidation.

The same effect is produced by heat. A glass bulb was attached by fusion to the neck of a retort, and a quantity of dry phosphorus placed both in the body of the retort and in the bulb; the extremity of the neck was connected with a glass tube more than 30 inches long, placed vertically, and with its lower end dipping under mercury. The neck of the retort above the bulb was filled with chloride of calcium, and a thermometer inserted through the tubulure. The apparatus being thus arranged, the phosphorus in the bulb was heated till it took fire, and thus absorbed all the oxygen contained in the air of the retort. The body of the retort was then heated to 100°, to drive off any moisture adhering to the phosphorus, and then left to cool. After this, the phosphorus was slowly heated. Sublimation began at 150°, but without change of colour. At 226° (439° F.), the phosphorus after a while assumed the colour of carmine; it likewise became thicker, and the colour continually increased in intensity, till at length perfect opacity was produced. This change of character was due to the separation of a red powder, which at first settled down to the bottom of the vessel, but rapidly increased in quantity till it extended through the whole mass. When the phosphorus was kept from 48 to 60 hours at a temperature between 240° and 250°, a solid stratum of amorphous phosphorus was formed at the bottom of the vessel, and above it a mixture of ordinary phosphorus with a considerable quantity of the amorphous variety. The change takes place, though slowly, at

* The term *Allotropy* has lately been brought into use to denote the different states in which the same substance may exist without alteration of chemical constitution: thus, diamond, graphite, and charcoal are allotropic conditions of carbon; the octohedral, prismatic, and plastic states are allotropic conditions of sulphur; &c. [W.]

215°; but it is most rapid between 240° and 250°. It is accelerated by the action of light. Under diminished pressure the conversion is slower, and does not appear to be produced at all when the pressure is reduced below 393mm ($15\frac{1}{2}$ in.).* Eight ounces of ordinary phosphorus heated for 50 hours in the manner above described yielded 6 oz. of amorphous phosphorus. The latter may be separated from ordinary phosphorus by digestion in bisulphide of carbon, which dissolves the ordinary but not the amorphous phosphorus. The undissolved portion must be collected on a filter, and thoroughly washed with bisulphide of carbon. For complete purification, the residue is to be boiled in caustic potash of density 1·3, and then washed, first with water slightly acidulated with nitric acid, and afterwards with pure water.

Amorphous phosphorus thus obtained is a soft powder destitute of crystalline structure, varying in colour between carmine and scarlet, sometimes even of a blackish-brown tint. When heated in a liquid, it becomes darker, and after some time acquires a deep violet colour. Its specific gravity at 10° is 1·964; that of ordinary phosphorus melted at 45° is 1·88, and in the solid state, 1·840....1·826. (Schrötter.) Amorphous phosphorus, by repeated distillation in an atmosphere of carbonic acid, is converted, *without loss of weight*, into ordinary phosphorus—a proof that it is really pure phosphorus, and not an oxide: the change takes place at 260° (500° F.). It is unalterable in the air, insoluble in bi-sulphide of carbon, alcohol, ether, rock-oil, and ter-chloride of phosphorus. Oil of turpentine, and other liquids of high boiling-point, dissolve small quantities of it when heated; but when deposited from them on cooling, it is re-converted into ordinary phosphorus. It does not shine in the dark till heated nearly to the point at which it takes fire (near 500° F.). Concentrated sulphuric acid has no action upon it in the cold—but, on the application of heat, dissolves it, with evolution of sulphurous acid. Nitric acid dissolves it readily. It decomposes many metallic oxides; *e. g.* the oxides of manganese, lead, silver, copper, and mercury, with the aid of friction or heat—sometimes with explosion.

It appears then that phosphorus, like sulphur and carbon, can exist in three allotropic conditions: (1) Ordinary transparent, nearly colourless phosphorus, which is really of crystalline structure—though that structure is not seen in phosphorus solidified in the ordinary way from a state of fusion, because in solidifying it passes through the viscid state, which is inimical to crystallization. (2) White, opaque phosphorus, already described (p. 107), produced by the action of light upon phosphorus under water: this is also a crystalline modification. (3) Red amorphous phosphorus, produced by the action of light or heat in the manner just detailed†. (Schrötter.)

* The limitation here spoken of must refer to the action of heat alone, without light; for in presence of light the change takes place even in the Torricellian vacuum. [W.]

† It is possible that even a fourth modification of this element may exist, viz., the yellow, semitransparent state which it always acquires when kept for some time under water. Napoli (*Compt. rend.* 64, 252,) remarks that the want of transparency here spoken of arises not from impurity, but from a peculiar state of molecular aggregation. This state may, however, be only intermediate between the transparent and the white opaque varieties (1) and (2). Wöhler (*Ann. Pharm.* 45, 249) states that either this yellow phosphorus or the red amorphous variety may be rendered colourless and transparent like glass, by fusing it in a concentrated solution of bichromate of potassa mixed with sulphuric acid. To ensure contact, the bottle should be closed and well shaken

The atomic weight of phosphorus has been lately determined by Pelouze to be 400·3 on the oxygen scale, or 32 on the hydrogen scale. ¶

Compounds of Phosphorus.

PHOSPHORUS AND OXYGEN.

A. PHOSPHORIC OXIDE. P^2O.

Red Phosphoric matter. Oxide of Phosphorus, Phosphoroxyd.

Formation. 1. When phosphorus—either in vacuo, or in hydrogen, nitrogen, carbonic acid, arsenuretted hydrogen, or marsh-gas, or in alcohol or water,—is exposed to colourless or violet light.—In vacuo and in the above-named gases, phosphorus first volatilizes, and then settles on the sides of the glass vessel, provided they are transparent, in the form of a brown-red substance.—In nitric oxide gas, phosphorus becomes covered, not with a red but with a white coating: in sulphide of carbon and sulphide of phosphorus also, phosphorus does not redden. The light of burning sulphur and of the Indian white fire likewise do not redden phosphorus. (Böckmann, A. Vogel.)—Whence the oxygen required for the formation of the oxide is derived, when the phosphorus is placed in the above-mentioned gases, is not clearly made out: it is probable, however, that, in the experiments just described, water was not completely excluded, and was converted by the phosphorus, under the influence of light, into phosphoric oxide and phosphuretted hydrogen. (See p. 108.) 2. When phosphorus, in contact with water or other compounds of oxygen, is passed through a red-hot tube, or when it is rapidly burnt in oxygen gas, common air, or rarefied air,—the phosphoric acid produced is mixed with phosphoric oxide. 3. By heating phosphorus with aqueous solution of iodic or hyperiodic acid (Benckiser), or with nitrate of ammonia. (Marchand.) 4. On exposing to the air a solution of phosphorus in terchloride of phosphorus or anhydrous ether.

Preparation. 1. Bubbles of oxygen gas are thrown upon phosphorus heated under water, so that vivid combustion ensues. (A. Vogel.)—The phosphoric acid produced in this combustion dissolves in the water; the flakes of oxide which swim about are washed and heated in a retort to free them from water and unoxidized phosphorus; they are then washed a second time to remove the newly formed phosphoric acid, and dried in vacuo over oil of vitriol. (Pelouze.) Böttger (*Ann. Pharm.* 29, 82) washes the oxide with water—agitates it briskly for a minute with a mixture of equal measures of bisulphide of carbon and absolute alcohol, which dissolves the phosphorus—decants—agitates the oxide a second time with a fresh quantity of the mixture,—collects it on a filter—washes it first with alcohol, then with water—and dries it, either in the open air, or under a glass jar with oil of vitriol. 2. Phosphorus spread in a thin

till the phosphorus divides itself into small globules: these reunite when the liquid is left at rest. Phosphorus thus treated generally remains liquid after cooling, but solidifies instantly when touched by any solid body. [W.]

layer over a porcelain capsule (in order that the temperature may not rise too high) is set on fire—the residue freed by water from phosphoric acid,—then dried and boiled with terchloride of phosphorus to remove unoxidized phosphorus—and finally washed with water and dried. (Leverrier.) 3. In a strong glass globe of the capacity of about a pint, and having a long and strong tube luted on to it, 5 grammes of phosphorus are heated and spread over the whole of the inner surface: a small quantity of nitrate of ammonia is then thrown in, and the part of the globe where it rests strongly heated over the flame of a spirit-lamp. As the salt decomposes, a red flame shoots out of the tube, and the whole of the globe becomes covered with phosphoric oxide. Should any of the phosphorus remain unoxidized, more nitrate of ammonia is introduced and heat again applied. After cooling, the flakes of oxide are rinsed out with water, and when thoroughly washed, they are heated in a retort filled with hydrogen gas to distil off the excess of phosphorus. (Marchand, *J. pr. Chem.* 13, 442.) 4. Phosphorus is boiled with solution of hyperiodic or iodic acid, or a mixture of hyperiodate of soda with dilute nitric acid, or of iodate of soda with dilute sulphuric acid, till it has lost its fluidity. The mixture of phosphorus and phosphoric oxide thus obtained is then rubbed to powder under water and again boiled in the acid liquid.—Iodine is set free in the process. (Benckiser, *Ann. Pharm.* 17, 258.) 5. Into a glass flask of the capacity of about a quart, and having a neck 4 inches long and one inch wide, there is introduced a small quantity of terchloride of phosphorus,—then some pieces of phosphorus weighing half a gramme and dried with paper, in sufficient quantity to form a layer ¼ of an inch thick,—then more terchloride, sufficient to partially cover the phosphorus. After twenty-four hours' exposure to the air, a thick white crust of phosphatic acid is formed on the surface where the access of oxygen is easiest; while below this and above the phosphorus, there is produced a yellow layer of *phosphate of phosphoric oxide*, the quantity of which attains its maximum in twenty-four hours' longer. The chloride of phosphorus, which may be used again for the same purpose, is then poured off, and the pieces of phosphorus to which the phosphate of phosphoric oxide adheres, separated from one another, and put singly into cold water, so that no rise of temperature, which would decompose the phosphate, may take place. The phosphate of phosphoric oxide dissolves in the water, forming a yellow solution which is poured off from the phosphorus and heated to 80°. It is thereby resolved into phosphoric acid which remains dissolved, and *hydrate of phosphoric oxide* which falls down in yellow flakes. The latter is quickly washed on a filter with warm water, transferred while yet moist into a porcelain dish, and dried in vacuo over oil of vitriol: it then also loses its water of hydration. If the air be slowly exhausted, the oxide remains in small, red, partly crystalline grains, which yield a yellow powder; if the exhaustion be rapidly made, so as to freeze the water, the hydrate gives up its water suddenly,—and when the ice is allowed to melt in the air, the oxide settles at the bottom in the form of a delicate yellow powder. The oxide thus obtained is free from chlorine and hydrogen. (Leverrier.) By proceeding in the same manner, with the exception of using perfectly anhydrous ether in place of chloride of phosphorus (if the ether contains water, nothing but phosphatic acid is produced), a yellow hydrate is obtained; and this, when dried under the air-pump, yields a dry orange-yellow compound of 90·3 phosphoric oxide and 9·7 organic matter, probably ether. This compound is not decomposed by boiling in water—

dissolves without residue in nitric acid,—and when heated alone or set on fire in the air, leaves a carbonaceous residue. (Leverrier.)

Phosphoric oxide must be kept in a dry atmosphere.

Properties. The oxide prepared according to (5) is a yellow powder, heavier than water, and so long as it remains dry, destitute of taste and smell. That prepared according to (1) acquires a red colour and loses the property of combining with alkalis, in consequence of the heat required to drive off the excess of phosphorus mixed with it; it likewise contains a somewhat greater quantity of oxygen. To obtain pure phosphoric oxide of a bright red colour, and not capable of combining with alkalis, the yellow oxide is kept for 10 hours at a heat of 300°. (Leverrier.)

	Calculation.		Leverrier (5)	Pelouze (1.)
2P	62·8	88·7	88·64	85·5
O	8	11·3	11·36	14·5
P^2O	70·8	100·0	100·00	100·0

(P^4O = 4 . 196·14 + 100 = 784·56, according to Berzelius.)

Decompositions. 1. The oxide heated apart from the air, above the boiling point of mercury, is rapidly decomposed into phosphorus which evaporates, and phosphoric acid which remains behind. (Pelouze, Leverrier.) $5P^2O = PO^5 + 9P$. 2. In dry air it may be heated to 300° without decomposing, and begins to burn at the temperature at which phosphorus also heated apart from the air begins to volatilize. (Leverrier.) 3. In damp air it oxidizes, exhaling a faint odour like that of phosphuretted hydrogen. 4. It rapidly takes fire in chlorine gas either dry or moist, phosphoric acid and chloride of phosphorus being produced. (Pelouze; Leverrier.) 5. It is decomposed by sulphur, the decomposition commencing at the melting point of that substance. 6. In contact with aqueous solutions of the alkalis, it is resolved into nearly pure phosphuretted hydrogen gas, and a phosphate of the alkali. If the quantity of alkali be smaller than is necessary to saturate the phosphoric acid which may be formed, part of the oxide remains undecomposed. Baryta and lime-water decompose the oxide more slowly, because they produce insoluble phosphates which form a crust round the oxide. (Leverrier.) Hydrochloric acid gas does not decompose the oxide, even with the aid of heat. (For the conversion of the oxide into phosphoric acid by oxidation, vid. *Formation of phosphoric acid.*)

Combinations.—*a.* With water:—*Hydrate of phosphoric oxide.* The preparation of this compound has been already given in describing that of the anhydrous oxide (5). The voluminous yellow mass cannot be dried, even at ordinary temperatures, without losing its combined water: hence the determination of its composition is uncertain. According to one experiment, it contains 79·5 (1 at.) phosphoric oxide and 20·5 (2 at.) water. It reddens litmus feebly even after being washed as completely as possible. It suffers scarcely any alteration by boiling with water; it is only after 48 hours' boiling that the hydrate loses a portion of its water, and the liquid becomes slightly acid. Exposed to the rays of the sun under water, it is converted somewhat rapidly into phosphoric acid and phosphuretted hydrogen gas. It is very slightly soluble in water, and imparts to that liquid the property of blackening copper-salts. (Leverrier.)

b. With phosphoric acid.

c. With salifiable bases. Phosphoric oxide, provided it has not been turned red by the application of a strong heat, blackens quickly in ammoniacal gas and in alkaline solutions, by taking up the alkali: acids turn it yellow again. These black compounds are slightly soluble in water, so that the filtrate blackens copper-salts; but in contact with water, they are quickly decomposed as described in (6). (Leverrier.)

Phosphoric oxide is insoluble in alcohol, ether, volatile oils and fixed oils. (Leverrier.)

B. Hypophosphorous Acid. PO.

Acide hypophosphoreux, Acidum hypophosphorosum, Unterphosphorige Säure.

Formation. 1. In the decomposition of phosphide of barium, strontium, or calcium, by water. (Dulong.) 2. When phosphorus is gently heated with hydrate of lime, or boiled with milk of lime, baryta-water, or aqueous or alcoholic solution of potassa. (H. Rose.) When aqueous solution of potassa is used, a large quantity of phosphoric acid is mixed with the hypophosphorous; with the alcoholic solution, the quantity of phosphoric acid produced is but small. (H. Rose.)

Not known in the separate state.

	Calculation.		H. Rose, Calc.	Dulong.
P	31·4	79·695	79·69	73·4
O	8	20·305	20·31	26·6
PO	39·4	100·000	100·00	100·0

($P^2O = 2 . 196{\cdot}14 + 100 = 492{\cdot}28$. Berzelius.)

Combinations.—*a.* With water.—*x. Hydrate of hypophosphorous acid.* 1. Phosphide of barium is decomposed by water,—the solution of hypophosphite of baryta thereby formed is filtered from the phosphate which remains undissolved—the baryta precipitated from the filtrate by sulphuric acid added in due proportion—and the liquid, after a second filtration, concentrated to the consistence of a syrup. (Dulong.) 2. Phosphorus is boiled with baryta-water till it disappears, and the vapour no longer has the odour of garlic; the baryta is precipitated from the filtrate by a slight excess of sulphuric acid,—the liquid again filtered—the filtrate agitated in the cold, and for a short time only, with protoxide of lead—the sulphate of lead removed by filtration—the lead precipitated from the liquid, which contains basic hypophosphite of lead, by hydrosulphuric acid gas—and the filtrate concentrated by evaporation. When the quantity of oxide of lead is too small, or when the liquid is heated, some of the oxide is reduced; when the liquid is suffered to remain too long in contact with it, an insoluble basic salt is formed. (H. Rose.)

The hydrate is a viscid, uncrystallizable, very acid liquid. (Dulong.) When heated, it is completely decomposed, together with the water of hydration, the products being the less inflammable phosphuretted hydrogen gas, and phosphoric acid which remains behind. (H. Rose.) $2PO + 3HO = PH^3 + PO^5$. The statement of Dulong, that phosphorus is volatilized at the same time, is contradicted by Rose.

β. With a larger quantity of water, the hydrate forms a thin colourless solution which precipitates the metals from solutions of gold and silver (Dulong); from a solution of corrosive sublimate it precipitates calomel or metallic mercury, according to the proportions used. (H. Rose.)

b. With salifiable bases, hypophosphorous acid forms salts called *Hypophosphites.—Preparation:* 1. By dissolving the bases in the aqueous solution of the acid. (Dulong.) 2. By boiling phosphorus in alcoholic solution of potassa. 3. By boiling phosphorus in solution of baryta, strontia, or lime, and filtering from the insoluble phosphate which is formed at the same time. 4. The lime-salt prepared according to (2) is precipitated by carbonate or sulphate of ammonia, potassa, or soda—the liquid evaporated to dryness—and the hypophosphite extracted by alcohol. 5. The lime-salt dissolved in water is boiled with an insoluble oxalate, as that of magnesia or protoxide of manganese. Many other oxalates decompose hypophosphite of lime, but not completely. (H. Rose.)

The hypophosphites are mostly crystallizable: they cannot exist without a certain quantity of water, which amounts to $1\frac{1}{2}$ atoms for each atom of the salt. (H. Rose.) Hence, for example, the formula of the baryta-salt deprived of water as much as possible is : $2(BaO,PO)+3Aq$. The salts when heated are converted—by decomposition of the water which essentially belongs to them—into phosphuretted hydrogen gas, generally of the easily inflammable kind, and a di-phosphate which remains behind. (Dulong; H. Rose.) $2BaO,2PO + 3HO = 2BaO,bPO^5 + PH^3$. Part of the phosphuretted hydrogen is resolved into hydrogen and phosphorus, the quantity thus decomposed increasing with the heat, being greater therefore when the salt is heated strongly and suddenly, than when it is cautiously heated, and greater towards the end of the operation, when little else than pure hydrogen is evolved, than at the beginning. Of all these salts, the lead salt yields the largest quantity of undecomposed phosphuretted hydrogen. The cobalt and nickel salts when heated decompose a somewhat greater quantity of water, and therefore evolve a gaseous mixture less rich in phosphorus, leaving a salt which contains rather more phosphoric acid. The residue which remains after the ignition of the hypophosphites contains a certain quantity of phosphoric oxide, which gives it a red colour (white, however, at the temperature of ignition) when the phosphate is essentially white, and black when the phosphate itself is coloured. (H. Rose.)

The hypophosphites, when dry, are permanent in the air; but in the state of solution they oxidize when boiled in contact with the air, and are converted into simple phosphates. $KO,PO + 4O = KO,PO^5$. (Dulong.) When boiled in a close vessel, they remain unaltered, provided no excess of alkali is present; but alkaline hypophosphites dissolved in water and containing excess of alkali, are decomposed by boiling into hydrogen gas and a residual alkaline phosphate, the change taking place with greater rapidity in proportion as the alkali is stronger, its quantity greater, and the solution more highly concentrated. (H. Rose.) In an alcoholic solution, the resolution of the hypophosphite into hydrogen gas and an alkaline phosphate does not take place so readily.

$$3KO + PO + 4HO = 3KO, PO^5 + 4H.$$

The aqueous solutions of these salts throw down metallic copper from solutions of copper salts, but only when highly concentrated, and at a high temperature. When mixed with hydrochloric acid, they precipitate calomel from a solution of proto-chloride of mercury in excess, and metallic mercury when the mercurial solution is not in excess. With nitrate of silver they give a white precipitate which soon turns brown and is converted into metallic silver, the change being further accelerated by the action of heat. From chloride of gold they precipitate the metal. (H.

Rose, *Analyt. Chem.* 1, 274.) All hypophosphites are soluble in water, several also in alcohol; some of them deliquesce in the air. (Dulong.) The solution does not precipitate baryta, strontia, or lime-water.

¶ All the hypophosphites contain at least 2 atoms of water: the hydrated acid in its most concentrated form, contains three, one of which is basic and may be replaced by a metallic oxide; while the other two are in a state of more intimate combination, and cannot be replaced by metallic oxides, but appear to be essential to the constitution of the acid, and are present in all its salts. The hydrate may therefore be denoted by $2HO,PO + HO$; and the general formula of a hypophosphite will be $(2HO,PO + RO + nAq)$. Hydrogen as well as oxygen appears then to be essential to the constitution of the acid. For this reason, Wurtz regards it as a compound of phosphorus, hydrogen, and oxygen, denoted by the formula PH^2O^3. On this hypothesis, the composition of the hydrate will be HO, PH^2O^3, and the general formula of a hypophosphite, $RO,PH^2O^3 + nAq$. In the compound PH^2O^3, both the hydrogen and oxygen may be regarded as electro-negative elements, and then the acid will be viewed as an analogue of phosphoric acid, PO^5, in which 2 atoms of oxygen are replaced by 2 atoms of hydrogen. Or again, the hydrogen and phosphorus may be regarded as positive, the oxygen as negative, and the acid, PH^2O^3, as a compound of oxygen with the compound radical PH^2. This radical has actually been isolated by Paul Thénard. (*Vid.* p. 133.) ¶

C. Phosphorous Acid. PO^3.

Unvollkommene Phosphorsäure, Phosphorige Säure, Acide phosphoreux, Acidum phosphorosum.

Formation. By the imperfect combustion of phosphorus. *a.* When phosphorus is placed, at a somewhat, elevated temperature, in contact with a small quantity of air sparingly renewed or very much rarefied.

b. When phosphorus is exposed to the air or to oxygen gas at ordinary temperatures. *Slow combustion of phosphorus.* This combustion is attended with a very slight degree of heat, a light visible only in the dark, and the formation of white fumes which smell like garlic. The phosphorous acid hereby produced condenses with the moisture of the air to a liquid, and, by taking up an additional dose of oxygen, is converted into a mixture of phosphorous and phosphoric acid.

Phosphorus exhibits slow combustion in the air when it is exposed, at ordinary pressures, to a temperature above 7° (44·6° F.). In rarefied air its luminosity increases with the degree of rarefaction, and the light does not diminish in brightness even in the vacuum of the air-pump: if air be then suddenly admitted, the light disappears. (J. Davy.) In compressed air, phosphorus does not shine till the temperature is raised. (Hellwig.) It does not shine in air compressed to four atmospheres. (J. Davy.)

In oxygen gas, under the ordinary atmospheric pressure, phosphorus does not exhibit slow combustion till heated to 27° (80·6° F.). (It behaved differently in oxygen gas prepared from chlorate of potassa at different times; at temperatures between 16° and 27°, it shone, sometimes not at all, sometimes more feebly than in air, sometimes very brightly, in flashes, a degree of heat being likewise produced sufficient to melt the phospho-

rus, but not to cause rapid inflammation. (J. Davy.) At a temperature at which it does not shine, it volatilizes unaltered in oxygen gas, and then produces luminosity on the introduction of nitrogen or hydrogen gas. When nitrogen, hydrogen, carbonic oxide, carbonic acid, or hydrochloric acid gas has been placed in contact with phosphorus and become loaded with its vapour, the introduction of oxygen gas produces an emission of light. (Berthollet; J. Davy.) In oxygen gas under a pressure of $1\frac{1}{2}$ atmospheres, phosphorus does not shine till it is heated to its melting point, and then it takes fire (J. Davy); on the other hand, it shines at ordinary temperatures in oxygen gas rarefied by the air-pump. (Schweigger; J. Davy.) The more therefore the oxygen is rarefied, either by diminution of external pressure or by mixture with other gases, nitrogen for example, the lower is the temperature at which the phosphorus begins to undergo slow combustion. (Schweigger, *Schw.* 40, 16.) It still remains to be explained why the rarefaction of oxygen gas facilitates the combustion.

According to Thénard, the slow combustion ceases in the course of an hour when the air or oxygen gas is dry, because the acid formed surrounds the phosphorus as a solid crust, and thus prevents further contact between the phosphorus and the gas: but when water is present, it is rapidly attracted by the acid, which then deliquesces and allows the combustion to go on. According to J. Davy, on the contrary, phosphorus burns in air thoroughly dried over oil of vitriol quite as rapidly as in moist air, until all the oxygen is consumed. According to the author's experiments, phosphorus emits no fumes in air dried over oil of vitriol, but still shines very feebly in the dark.

The luminosity of phosphorus in the air is not prevented by the presence of the gas or vapour of sulphur, hydrochloric acid, ammonia, or acetic acid. (J. Davy; Graham.) Phosphorus shines even in hydrochloric or carbonic acid gas containing but a trace of air. On the other hand, the luminosity is prevented by phosphuretted hydrogen, sulphuretted hydrogen, sulphurous acid gas, vapour of sulphide of carbon, vapour of iodine, (according to J. Davy this last vapour stops the phosphorescence; according to Graham, it does not), chlorine gas, nitrous oxide gas, vapour of hyponitric acid, marsh-gas, olefiant gas, or the vapour of ether, alcohol, rock-oil, oil of turpentine, eupion, creosote, and other volatile oils. (J. Davy; Graham; Vogel.) Many but not all of these substances form compounds with phosphorus, which are but little inclined to the slow combustion.

Phosphorus does not shine at 21° in air which contains $\frac{1}{1000}$ of its volume of phosphuretted hydrogen gas not spontaneously inflammable. (Graham.) At 10°, less than $\frac{1}{15}$ of a volume of sulphurous acid gas is sufficient to prevent the luminosity of phosphorus in the air, but at 18° it shines again and fuses. (Vogel.) [In consequence of the formation of sulphide of phosphorus?] Of sulphide of carbon, less than a drop is sufficient to prevent the luminosity of phosphorus in 25 cubic inches of air at 10°, and even at the melting point; and the phosphorus then no longer shines in a fresh portion of air, unless it has been previously washed and dried with bibulous paper. (Vogel.)—$\frac{1}{3}$ of a volume of hydrosulphuric acid gas, or $\frac{1}{4}$ of chlorine added to 1 volume of air prevents phosphorus from shining in it. (Graham.) Vapour of bromine at 10° merely weakens the luminosity of phosphorus in the air, but does not completely destroy it: at 18°, phosphorus fuses in air charged with bromine, but does not take fire. Of chlorine gas at least 8 measures are required for

every 100 measures of air at 12·5°, to stop the phosphorescence. When air is mixed with $\frac{1}{5}$ or $\frac{1}{6}$ of its volume of chlorine gas, phosphorus melts in it at 8° in consequence of the formation of chloride of phosphorus, and at the same time becomes so much heated that it takes fire. (Vogel.) In a mixture of air and nitrous oxide gas, phosphorus may be heated above its melting point without emitting light, but it takes fire at its boiling point. In air containing a trace of hyponitric acid, phosphorus does not shine. Marsh-gas retards the slow combustion, but does not altogether prevent it. Even $\frac{1}{450}$ of a volume of olefiant gas mixed with one volume of air destroys the luminosity at a temperature of 15° and under the ordinary atmospheric pressure; and $\frac{1}{400}$, even at 21°. In a mixture of air and olefiant gas, phosphorus may even be heated to 100° without taking fire. When the external pressure is diminished, the interfering power of olefiant gas becomes less; phosphorus shines at 21° in a mixture of equal volumes of olefiant gas and air at 0·5 English inches external pressure; of 1 volume of olefiant gas with 2 volumes of air, at 1·4 in.; with 4 volumes of air, at 2·3 in.; with 9 volumes of air, at 2·2 in.; with 19 volumes of air, at 5·0 in.; with 29 volumes, at 10·3 in.; with 39 volumes ,at 12·1 in.; with 49 volumes, at 16·5 in.; with 99 volumes, at 25·5 in.; with 199 volumes, at 26·5 in.; and with 449 volumes of air, at 29·0 in. (Graham.) Coal-gas likewise stops the phosphorescence (Graham); so likewise does hydrogen gas prepared from vapour of water and red-hot iron filings, its action being due to vapour of oily matters mixed with it; for that prepared by means of harpsichord wire produces no such effect. (J. Davy.) In air impregnated with vapour of alcohol, phosphorus does not shine at 26·7°. (Graham.) Phosphorus shines at 19° in air with which is mixed $\frac{1}{150}$ of its volume of ether vapour, $\frac{1}{1820}$ of vapour of sulphide of carbon, or $\frac{1}{4444}$ of vapour of turpentine. In a mixture of 3 measures of air and 2 measures of ether vapour, phosphorus emits a faint light visible only in the dark, commencing at 104·7°, and always ceasing when the temperature falls to 99°: rapid combustion begins at 115·5°. In a mixture of 111 volumes of air and 1 volume of vapour of rock-oil, phosphorus begins to shine at 67·7°; and in a mixture of 116 volumes of air, and 1 volume of vapour of turpentine, at 83·5°. But the vapours of rock-oil and oil of turpentine rapidly lose their interfering power when the external pressure is diminished. The oil deposited by compressed oil-gas likewise exerts a preventive action. (Graham.) Vapour of eupion, and still more that of creosote, mixed in small quantity with air, weakens or stops the emission of light. (Vogel.) Camphor vapour mixed with air produces no effect, according to Graham, but according to J. Davy, it stops the phosphorescence. (*Comp.* Berthollet, *J. Polytechn. Cah.* 3, p. 275; J. Davy, *N. Ed. Phil. J.* 15, 48; also *Schw.* 68, 384; also *Ann. Pharm.* 9, 158; Graham, *N. Quart. J. of Sc.* 6, 83; also *Schw.* 57, 230; *abstr. Pogg.* 17, 375; Vogel, Jun. *J. pr. Chem.* 19, 394.)

2. By dissolving phosphorus in heated nitric acid. Phosphoric acid is produced at the same time, the quantity increasing with the strength of the acid.

3. In the mutual decomposition of water and terchloride of phosphorus. (*Sch.* 40.)

Preparation. When phosphorus is heated to 100° in a narrow glass tube containing air it sublimes as phosphorous acid, a small quantity of phosphoric oxide being produced at the same time. (Steinacher, *A. Gehl.* 1,681.)—Berzelius (*Lehrb.* 2, 67) conducts this process in the following

manner. One end of a glass tube 10 inches long and half an inch wide, is nearly closed at one end, leaving however an aperture of the size of a large pin; it is then bent at an obtuse angle at the distance of from half an inch to an inch of the closed end; a piece of phosphorus is introduced and placed near the narrow aperture and heated from time to time: it then burns with a pale greenish flame, and forms phosphorous acid, which condenses in the part of the tube directed upwards.—2. Phosphorus heated in highly rarefied air, forms phosphoric acid, phosphorous acid, and phosphoric oxide. (H. Davy.)

Properties. Phosphorous acid forms white and very bulky flakes, easily volatilized and sublimed; smells like garlic; has a sour and characteristically sharp taste; reddens moistened litmus paper strongly, but not that which is dry. (Steinacher.)

	Calculation.		Davy.	Berzelius.	Dulong.	Thomson.
P	31·4	56·68	56	56·524	57·18	60
3O	24	43·32	44	43.476	42·82	40
PO^3	55·4	100·00	100	100·000	100·00	100

($P^2O^3 = 2 . 196·14 + 3 . 100 = 692·28$. Berzelius.)

Decompositions. 1. The hydrated acid undergoes decomposition at a certain degree of concentration, and the water being likewise decomposed, the products are phosphuretted hydrogen gas of the less inflammable variety, and hydrated phosphoric acid which remains behind: hence the acid when heated in the air exhibits vivid combustion, evolving bubble of gas which take fire as they escape. (H. Davy.)

$$4PO^3 + 9HO = 6HO, 3PO^5 + PH^3.$$

2. When zinc or iron is dissolved in the acid, phosphuretted hydrogen gas and a salt of phosphoric acid are likewise produced. (Berzelius).—3. By sulphurous acid (*q. v.*).

Combinations. a. With water.—The anhydrous acid attracts the moisture of the air with so great a development of heat that it takes fire.

α. Hydrate of Phosphorous Acid. Terchloride of phosphorus is decomposed by water, and the hydrochloric acid produced, together with the excess of water, driven off by gentle evaporation. (H. Davy.) Instead of preparing the chloride of phosphorus beforehand, it is better to fill a cylinder 12 inches long, and at most an inch in diameter, one-fourth with phosphorus and three-fourths with water—heat it till the phosphorus melts—and then pass chlorine gas washed with water slowly into the liquid through a tube reaching down to the bottom of the cylinder. The chlorine sets fire to the phosphorus, combines with it, and forms terchloride of phosphorus, and this compound is decomposed by the superincumbent water. The water when saturated with acid must be replaced by fresh water, and more phosphorus added; for when the quantity of the latter is too small, pentachloride of phosphorus is formed and converted into phosphoric acid. (Droquet, *J. Chim. Med.* 4, 220, abstr. *Pogg.* 12, 268.)

After being concentrated as much as possible in a retort out of contact of air, or in vacuo over hydrate of potassa, the hydrate remains in the form of a thick uncrystallizable syrup containing 74·26 acid and 27·54 water. This, when gradually heated, is resolved into 71·62 per cent. of phosphoric acid, 8·91 of phosphuretted hydrogen, and 19·47 of

water; but when rapidly concentrated and to a greater extent, it yields 68·04 phosphoric acid, 10·27 phosphuretted hydrogen and 21·69 water.

β. Crystallized Phosphorous Acid. Formed by evaporating the solution to a thinner syrup than that above mentioned, and cooling it (H. Davy)—or by adding a small quantity of water to the hydrate. (H. Rose.) The crystals when heated yield 77 per cent. of hydrate of phosphoric acid together with 23 per cent. of phosphuretted hydrogen and water. (H. Davy.)

γ. Aqueous Phosphorous Acid. The crystallized acid deliquesces in the air, producing a colourless liquid which exceeds water in consistence and specific gravity: this liquid when concentrated must be preserved in close vessels. The solution precipitates the metals from chloride of gold, nitrate of silver, and protochloride of mercury,—or calomel from the latter, when the mercurial solution is in excess.

b. With various salifiable bases, phosphorous acid forms salts called *Phosphites;* but with many metallic oxides it is incapable of combining, because it reduces them. The affinity of phosphorous acid for salifiable bases is but small. The soluble phosphites have a somewhat sharp taste, like garlic. According to Graham, the normal salts contain one atom of acid to three atoms of base; but, according to H. Rose, most of the phosphites contain one atom of acid to two atoms of base; and others, one atom of acid to one atom of base. It appears also that they cannot be obtained in the anhydrous state. When heated, they are all, together with the water which they contain, resolved into hydrogen which escapes as gas, and a phosphate which remains behind; hence, when heated in contact with the air, they burn either with glow or with flame. Most of the phosphites when thus decomposed yield pure hydrogen gas; *e. g.*

$$2BaO, PO^3 + 2HO = 2BaO, PO^5 + 2H;$$

in others, a small quantity of phosphorus is mixed with the hydrogen. The phosphites of protoxide of manganese and oxide of lead, which when thoroughly dried do not contain sufficient water to effect this decomposition, are resolved into a mixture of much hydrogen with a small quantity of phosphuretted hydrogen gas, and a compound of 10 atoms of base with 4 atoms of phosphoric acid.

$$10PbO, 5PO^3 + 5HO = 10PbO, 4PO^5 + PH^3 + 2H.$$

Part of the PH^3 is resolved by the heat into its elements; hence phosphorus likewise sublimes. (H. Rose.)

At ordinary temperatures, the phosphites do not attract oxygen from the air; but they are oxidized and converted into phosphates by nitric acid, by chlorine water, by many metallic oxides, which are at the same time reduced,—and at higher temperatures, by salts of chloric and nitric acid with which they detonate. (*Vid.* Guy-Lussac, *Ann. Chim. Phys.* 1, 212.) They are not altered by boiling with solution of caustic potassa,—neither do they produce any evolution of hydrogen gas. They precipitate the metal from aqueous solution of protochloride of copper, but only on boiling. (H. Rose.) From solution of corrosive sublimate they precipitate calomel, and from nitrate of silver and chloride of gold they throw down metallic silver and metallic gold—the former being brown-black when precipitated from a cold solution, and black when precipitated at a boiling temperature. Many simple phosphites are insoluble in water, but are rendered soluble by excess of acid. Those which are soluble in water precipitate baryta and lime-water, as well as the salts

of the earthy alkalis, the earths, and the heavy metallic oxides (the lead-salts most easily of all),—sometimes even in the cold, sometimes, especially when the solutions are very dilute, only on the application of heat. They do not precipitate a mixed solution of sulphate of magnesia, sal-ammoniac, and ammonia, when diluted to a certain extent. This character distinguishes the phosphites from the phosphates. (H. Rose.)

¶ According to Wurtz, the phosphites are all bibasic, and all contain at least one atom of water (or rather of the elements of water). The hydrogen and oxygen thus united with a phosphite are never evolved in the form of water on the application of heat; neither can they be replaced by an atom of a metallic oxide. The crystallized hydrate of phosphorous acid contains 3 atoms of water, two of which are basic and may be replaced by two atoms of metallic oxide; but the third is inseparably bound up with the acid and is essential to its existence as an acid. Hence (as in the case of hypophosphorous acid) phosphorous acid may be regarded as a compound of phosphorus, hydrogen, and oxygen, denoted by the formula PHO^4—or as phosphoric acid in which one atom of oxygen is replaced by hydrogen. According to this view, the formula of the crystallized hydrate will be $2HO, PHO^4$; and the general formula of a phosphite:

$$2RO, PHO^4 + n\,Aq.$$

To this view of the composition of anhydrous phosphorous acid, it may be objected that the compound PO^3 has actually been isolated (p. 117). But the properties of this and of the other so-called anhydrous acids, such as SO^3, SO^2, PO^5, &c., which Gerhardt calls *Anhydrides*, are altogether different from those of the corresponding hydrated compounds. In fact it would appear that the presence of the elements of water, or at least of hydrogen, is essential to the development of acid properties properly so called—and that the *Anhydrides* are not really *acids* in the true sense of the word. The existence of PO^3 in the separate state need not, therefore, be regarded as subversive of the preceding view of the constitution of phosphorous acid. (Wurtz, *Ann. Pharm.* 58, 49.) ¶

c. With alcohol and other organic liquids.

Pelletier's Phosphorous acid, Hypophosphoric acid, Phosphatic acid.—This compound is obtained by the slow combustion of phosphorus.—Pelletier's method of preparing it (*Crell, Ann.* 1796, 2, 447) is to introduce a number of separate sticks of phosphorus into glass tubes an inch long, open above and below, but drawn out funnel-shape at bottom—these tubes being arranged in a funnel, and the funnel inserted into a bottle which stands in a dish containing water. The whole arrangement is covered with a glass bell-jar, but in such a manner as to give access to the external air—which, however, ought not to be very warm, as in that case the phosphorus would melt and take fire. The acid which collects in the bottle is equal in weight to three times the quantity of phosphorus consumed, but it may be obtained in a more concentrated state by gentle evaporation. Bucholz lays the sticks of phosphorus on the upper part of an inclined shallow dish, and places the dish in a cellar at a temperature not exceeding 50° F. The acid produced, which amounts to more than five times the weight of phosphorus used, flows down into the lower part of the dish. The aqueous acid thus obtained presents the character of a dense tenacious syrup of faint garlic odour and very acid taste; it evolves phosphuretted hydrogen when

heated, and combines with larger quantities of water, producing considerable rise of temperature. Phosphorus containing arsenic yields phosphatic acid contaminated with arsenious acid, which is immediately precipitated by sulphuretted hydrogen: the acid when treated with zinc and hydrochloric acid, evolves arseniuretted hydrogen, and when heated alone till phosphuretted hydrogen is evolved, deposits the arsenic in black metallic laminæ. (A. Vogel, *J. pr. Chem.* 13, 55.) This acid of Pelletier may be regarded either as a particular degree of oxidation of phosphorus occupying an intermediate place between phosphorous and phosphoric acid, or else as a mere mixture of those two acids.

	Calculation.		Thénard.	Dulong.	or	Calculation.	
2P	62·8	46·59	47	47·85	PO^3	55·8	16·34
9O	72	53·41	53	52·15	$4PO^5$	285·6	83·66
P^2O^9	134·8	100·00	100	100·00	P^5O^{23}	341·4	100·00

In support of the former view it may be alleged that, according to Dulong, this acid always contains the same quantity of oxygen, and when exposed to the air even for a considerable time, does not appear to be converted into phosphoric acid by further oxidation. Since, however, when combined with salifiable bases, it does not form salts of a peculiar kind, but merely phosphites and phosphates, the latter view must be regarded as the more probable. The phosphorous acid first produced by the slow combustion of phosphorus appears to go on taking up more oxygen till four atoms of phosphoric acid are produced for each atom of phosphorous acid remaining. Leverrier (*Ann. Chim. Phys.* 65, 278), thinks it possible that phosphatic acid may be a compound of phosphoric acid and phosphoric oxide.

D. Phosphoric Acid. PO^5.

Acid of Bones, Acide phosphorique, Acidum phosphoricum, Phosphorsäure.

Sources. In the mineral kingdom, this acid occurs in combination with lime, magnesia, protoxide of cerium, yttria, alumina, and the oxides of uranium, manganese, iron, lead and copper; in various rocks of igneous origin (Fownes; Sullivan); in all primitive rocks (R. D. Thomson); in the organic kingdoms, especially in the animal, combined with ammonia, potassa, soda, lime, magnesia, and iron. All phosphates in the mineral kingdom contain ordinary phosphoric acid. (Boussingault, *Ann. Chim. Phys.* 55, 185.) The conclusion that they cannot therefore have been formed at a high temperature, is however inadmissible with regard to those which contain one atom of acid to 3 atoms of base.

Phosphorus exhibits rapid combustion under the following circumstances, the surrounding medium being at the ordinary temperature.

α. When considerable quantities of air are presented to the phosphorus —slow combustion taking place at first and producing a slight elevation of temperature—this rise of temperature accelerating the slow combustion —this in its turn raising the temperature still higher, and so on—till the phosphorus attains the temperature necessary for rapid combustion. According to Hünefeld (*J. pr. Chem.* 7, 233), a piece of phosphorus, loosely wrapped in soft white blotting-paper (which perhaps prevents the cooling), or laid with the freshly cut surface in contact with the paper—takes fire in a few minutes at a temperature of 20° (58° F.), after previously fusing at the corners.

β. The more finely the phosphorus is divided, either by itself or by mixture with other bodies of a pulverulent nature—the more quickly therefore the gradual combustion can go on, by the action of an increased surface of contact—the more quickly does the phosphorus take fire. Finely granulated phosphorus rapidly takes fire in the air after drying. Paper saturated with solution of phosphorus in bisulphide of carbon, takes fire after the evaporation of the latter, because the phosphorus remains on the paper in a fine state of division. Many of the preparations known by the name of *Phosphorus-boxes* are also formed on similar principles. They often likewise contain substances which absorb moisture from the air, and thereby produce a rise of temperature which favours the combustion. The following are mixtures of this kind: Phosphorus is heated above its boiling point in a small glass flask, and air is several times blown in with the blow-pipe, while the contents of the flask are constantly agitated. In this manner a red mixture of phosphorus, phosphoric oxide, phosphorous acid and phosphoric acid is produced. These acids, by their powerful attraction for moisture, favour the combustion of the phosphorus. The phosphoric oxide merely exerts a mechanical action, serving to divide the phosphorus. Melting phosphorus mixed with phosphoric oxide likewise, according to Pelouze (*J. Chim. Med.* 8, 533), yields a luminous mixture. Luminous mixtures are likewise obtained by heating phosphorus in a small flask together with calcined magnesia or pounded quicklime till it melts, the materials being well shaken up all the while. Saltzer (*Kastn. Arch.* 19, 120) melts in a small flask 30 grains of phosphorus with 10 grains of wax—blows air in with the bellows till the phosphorus takes fire, and, in consequence of the higher temperature thus produced, mixes more intimately with the wax—and then closes the flask. Benedix (*Schw.* 60, 129) fuses and works together, 1 part of fine cork-powder, 1 part of bees-wax, 4 of phosphorus, and 8 of rock-oil, which must be free from turpentine. The mass takes fire spontaneously at 20°; at lower temperatures, it is necessary to breathe upon it.

γ. The more the air is rarefied, the more energetic is the gradual combustion, and the more easily does it pass into rapid combustion, especially when the phosphorus is surrounded with floculent substances which prevent its cooling. When phosphorus is covered with cotton, or with pounded resin or sulphur, and the surrounding air rapidly abstracted by the air-pump, the phosphorus takes fire at ordinary temperatures. (Van Marum, *Gren. N. J. de Phys.* 3, 96, and Van Bemmelen, *A. Gehl.* 2, 252, *N. Gehl.* 1, 144, and *Gilb.* 59, 268. Meylink, *Repert.* 46, 489.) According to Bache (*Sill. Am. J.* 18, 372; also *Pogg.* 23, 151; also *Schw.* 63, 487) there is no necessity for surrounding the phosphorus with these different powders, in order to cause it to take fire on rarefying the air: nevertheless these powders facilitate the inflammation—not only those of sulphur or resin, but likewise those of charcoal, boracic acid, hydrate of potassa, hydrate of baryta, lime, carbonate of lime, magnesia, sal-ammonia, common salt, chloride of calcium, nitre, fluor spar, silica, arsenic, antimony, manganese, &c. Animal charcoal and lamp-black act so powerfully (by preventing cooling) that phosphorus sprinkled with them takes fire at 15·5° (60° F.) even in the open air.

On the other hand, the inflammation is retarded by increase of external pressure. When phosphorus is heated in a closed retort till it takes fire, the increased pressure produced by the heat causes the extinction of the flame; on opening the retort, the flame again appears. (J. Davy.)

Formation. 1. From phosphorus. *a.* Phosphoric acid is produced in the rapid combustion of phosphorus, provided a sufficient quantity of air or oxygen gas is present. The rapid combustion takes place at 60° (140° F.), producing a yellow flame in common air, and a dazzling white light accompanied by intense heat, in oxygen gas. The product is phosphoric acid, which partly rises in a white cloud luminous in the dark, partly remains in a glassy condition mixed with phosphoric oxide, at the place where the phosphorus burns. According to Davy, phosphorous acid is often produced at the same time.

b. Phosphorus is converted into phosphoric acid by abstracting oxygen from the following substances. From carbonic acid combined with a fixed alkali, the action being attended with moderate inflammation (a piece of phosphorus is placed at the closed end of a glass tube, and a fixed alkaline carbonate in the middle; the latter is heated to redness, and then the phosphorus converted into vapour by the application of heat); from concentrated sulphuric acid, hypochlorous and chlorous acid, nitrous oxide, nitric oxide, hyponitric and nitric acid, also from the salts of iodic, hyper-iodic, bromic, chloric, hyperchloric, and nitric acid, and from most metallic oxides and metallic acids,—the products of the decomposition being a phosphide of the metal and a phosphate of the oxide.

2. From phosphoric oxide. This substance oxidizes slowly in moist air, takes fire when heated to 300° (572° F.), and is converted into phosphoric acid by oil of vitriol, nitric acid, chlorate or nitrate of potassa, oxide of copper, and the salts of sesqui-oxide of iron, oxide of copper, and oxide of silver. (Pelouze; Leverrier.)

3. From hypophosphorous acid, which is converted into phosphoric acid both by heating (p. 113), and by contact with aqueous solution of iodine or chlorine, with hypochlorous or nitric acid, and with oxide of mercury, gold, or silver.

4. From phosphorous acid. By burning the anhydrous or the concentrated acid in the air (p. 118); by continued exposure of the dilute acid to the air; by oil of vitriol, chlorine, hypochlorous acid, nitric acid, and by salts of mercury, silver, and gold.

Preparation.—The only method of obtaining phosphoric acid in the anhydrous state is by the rapid combustion of phosphorus in dry air or oxygen gas.

1. A few grains of phosphorus are set on fire in a porcelain capsule standing on a dish, and covered with an inverted bell-jar of the capacity of 200 or 300 cubic inches: the flakes of acid produced are deposited on the sides of the jar and on the dish. By renewing the air, fresh quantities of phosphorus may be burnt. (Berzelius, *Lehrb.* 2, 59.)

2. A glass globe with three apertures, two at the sides and one at the top, is connected by one of the lateral apertures with a wide glass tube filled with chloride of calcium and open to the air at the other end; into the other horizontal aperture is fitted a bent glass tube which passes into one of the mouths of a Woulfe's bottle. From the other mouth of this bottle a tin tube proceeds vertically upwards, and is surrounded by a wider tin tube perforated with holes, so that it may be heated by means of red-hot charcoal placed in the outer tube. The heat thus applied produces a continuous draught of air through the chloride of calcium tube into the globe, and thence through the Woulfe's bottle into the tin tube. Lastly, to the third opening of the globe situated at the top is adapted a

porcelain tube; and from the lower extremity of this is suspended a small dish, in which the phosphorus, thrown in from time to time by the upper end of the tube (which can be closed by a stopper) is to be burnt. When a sufficient quantity of phosphorus has been consumed, the three tubes are removed from the apertures of the globe, the apertures closed, the acid shaken loose from the sides, and quickly introduced into a dry, well stopped glass vessel. (Delalande, *Ann. Chim. Phys.* 76, 117, also *J. pr. Chem.* 23, 300.)

3. A porcelain crucible is placed on a large dish of the same material, and on the crucible is laid a small porcelain capsule containing some pieces of phosphorus: a large tubulated bell-jar is placed over the whole. Through the cork which closes the opening there passes a narrow bent tube, and likewise a wide straight tube which descends into the interior of the jar. The bent tube serves to introduce a supply of oxygen gas evolved from chlorate of potassa, or contained in a gas-holder, and previously dried by chloride of calcium. Through the straight tube a red-hot wire is passed for the purpose of setting fire to the phosphorus; and, when the first portion is burnt away, fresh pieces are dropped in to supply its place. If the glass globe becomes too hot, the process is interrupted for a time. The floculent acid, which weighs more than twice as much as the phosphorus used, is scraped together with a spoon and put into a bottle. (Marchand, *J. pr. Chem.* 16, 373.)

4. Phosphorus is placed upon a porcelain dish and covered with a funnel having a hole in its side, through which the phosphorus can be set on fire, and fresh pieces introduced. The funnel is connected by a bent tube with a Woulfe's bottle containing water, and communicating by means of a second tube with an aspirator (p. 35), by which a draught of air is kept up. The acid, which is mixed with phosphorous acid, accumulates under the funnel and in the bent tube. (Brunner, *Pogg.* 38, 267.)

Properties. The acid which sublimes during the combustion presents the aspect of white flakes; that which remains where the phosphorus is burnt, forms a vitreous mass. It fuses at a red heat, and, according to Davy (*Ann. Chim. Phys.* 10, 218), sublimes below a white heat. It is inodorous; not corrosive; of strong and agreeable sour taste; and reddens litmus strongly. With baryta, strontia, or lime-water, it produces white flakes which dissolve in an excess of the acid.

	Calculation.		Lavoisier.	Thomson.	H.Davy.	Berzelius.	Dulong.	Valentine Rose.
P	31·4	43·98	39·35	42·86	42·6	43·936	44·923	46·5
5O	40	56·02	60·65	57·14	57·4	56·064	55·077	53·5
PO^5	71·4	100·00	100·00	100·00	100·0	100·000	100·000	100·0

($P^2O^5 = 2 . 196·14 + 5 . 100 = 892·28$. Berzelius.)

Phosphoric acid is decomposed by charcoal at a red heat, with formation of carbonic oxide; by potassium, sodium (by these with inflammation), zinc, iron, and some other metals, the products being a metallic phosphide and an oxide of the metal or phosphate of the oxide.

Combinations. Phosphoric acid occurs in three isomeric (or polymeric?) states (I., 109; II., 16), as Metaphosphoric or *a*-Phosphoric acid = aPO^5, one atom of which takes up only one atom of base; as Pyrophosphoric or *b*-Phosphoric acid = bPO^5, which combines with 2 atoms of base;

and as ordinary or *c*-Phosphoric = cPO^5, which requires 3 atoms of base. The acid obtained by the rapid combustion of phosphorus is the metaphosphoric; the other two varieties are not known in the separate state, but only in combination with water or with bases. The particular state in which the acid may exist depends upon the quantity of water or base with which it is united. If no base or water is present, or if the acid is combined with only one atom of it, the variety produced is the metaphosphoric acid; this, when 2 atoms of base are present, especially at high temperatures, is converted into pyrophosphoric—and with 3 or more atoms of base, into ordinary phosphoric acid. Conversely, the last two varieties, by abstraction of water or base, are converted into the first.

These diversities may be explained on the hypothesis either of isomerism, or of polymerism. (I., 109.) The atoms of oxygen and phosphorus appear to dispose themselves in different ways according to the number of atoms of water or of base presented to them, and thus to form acids of various degrees of saturating power. According to Graham's view (*Ann. Pharm.* 28, 19), on the other hand, there is but one kind of phosphoric acid. When this acid is intimately combined with only one atom of water, it can likewise take up by substitution (I. 37) only one atom of base; whereas, when intimately combined with 2 or 3 atoms of water, it can take up 2 or 3 atoms of base in their stead. But why does the anhydrous acid, when dissolved in a large quantity of water, unite intimately with but one atom of that substance, and not with two or three, unless it exists in a peculiar condition?

a. Combinations with water.

Hydrate of Metaphosphoric Acid. Glacial Phosphoric Acid. The aqueous solution of either of the three acids is evaporated in a platinum crucible till the quantity of water in the residue no longer diminishes. With the last portions of water, a quantity of acid likewise volatilizes. The syrupy liquid solidifies, on cooling, to a transparent glass which volatilizes altogether at a red heat.

	Calculation.		H. Rose.		Peligot.	Dulong.	Berthollet (*nearly*)
aPO^5	71·4	88·81	92·7	90·52	87·45	82·92	75
HO	9·0	11·19	7·3	9·48	12·55	17·08	25
HO, aPO^5	80·4	100·00	100·0	100·00	100·00	100·00	100

The diversities in the amount of water found in these several analyses are to be attributed to the different degrees to which the evaporation was carried. Berthollet's hydrate appears to have been that of pyrophosphoric acid. Peligot had heated his hydrate to redness. Rose's analyses show that, after rapid evaporation, there remains a mixture of hydrated and anhydrous acid.

Solution of Metaphosphoric Acid. The anhydrous acid obtained by combustion rapidly deliquesces in the air. It dissolves in water with disengagement of heat; but the flakes do not dissolve entirely in less than an hour. The hydrate deliquesces in the air. According to Berzelius, when water is poured upon this substance, it splits with violence into small pieces, which are projected upwards: solution takes place but slowly. The same solution is obtained when metaphosphate of soda dissolved in water is precipitated by acetate of lead, the metaphosphate of lead diffused through water and decomposed by sulphuretted hydrogen, and the liquid filtered. (Graham.) This solution gives white precipitates with chloride of barium or calcium, nitrate of silver, and solution of

white of egg: it likewise, according to Graham, throws down a difficultly soluble salt from solution of potassa. One part of anhydrous phosphoric acid dissolved in 10,000 parts of water reddens litmus, and gives an immediate precipitate with lime-water or acetate of lead; with one part of acid in 20,000 parts of water, the precipitate does not appear for half an hour. (Harting, *J. pr. Chem.* 22, 48.) After standing for several days, and more quickly when boiled, the solution (according to Graham) loses these properties, and is converted at once into ordinary phosphoric acid, not first into pyrophosphoric acid; because the water acting in excess induces the acid to assume the state in which it is capable of taking up the largest quantity of water (3 atoms).

Hydrate of Pyrophosphoric acid. By evaporating a solution of ordinary phosphoric acid in a platinum flask till the temperature rises to 213° (415° F.), an acid is obtained containing 23 per cent. ($2\frac{1}{2}$ at.) of water. (*Vid. seq.* Graham.) In this state it may take the form of a soft glass.—Peligot obtained it in opaque, indistinct crystals like loaf-sugar. Fused phosphoric acid was left to itself in a bottle for several years, and, by absorbing water, formed at the top transparent crystals of ordinary phosphoric acid, in the middle a mother liquid of 1·7 sp. gr., and at the bottom crystals of hydrated pyrophosphoric acid like those above mentioned. (*Ann. Chim. Phys.* 73, 286; also *J. pr. Chem.* 21, 169.)

	Calculation.		Peligot.
bPO^5	71·4	79·87	76·97
2HO	18	20·13	23·03
2HO, bPO^5	89·4	100·00	100·00

The crystals examined were still mixed with a portion of the hydrate of ordinary phosphoric acid. (Peligot.)

Solution of Pyrophosphoric acid. Pyrophosphate of soda dissolved in water is precipitated by acetate of lead; the precipitated pyrophosphate of lead is washed, diffused through water, and decomposed by hydrosulphuric acid, and the solution filtered from sulphide of lead. This solution gives a white, earthy precipitate with nitrate of silver, but does not precipitate chloride of barium or calcium, or solution of white of egg. The aqueous solution of this acid, even when dilute, remains unaltered for half a year, according to Graham; but when heated, it is converted into ordinary phosphoric acid.

Hydrate of ordinary Phosphoric acid; Crystallized Phosphoric acid. Aqueous solution of ordinary phosphoric acid, evaporated to a thin syrup and left at rest, crystallizes, according to Süersen (*Scher. J.* 8, 125), Steinacher (*A. Gehl.* 1, 577), and Stromeyer (*Grund. d. theor. Chem.* 1, 248), in right, four-sided prisms, slightly inclined, or in broadly flattened six-sided prisms, terminated with quadrilateral summits, and having planes of cleavage parallel to the lateral faces of the rhombic prism. The crystals are perfectly transparent, hard, and brittle.

	Calculation.		Brandes.	Peligot.
cPO^5	71·4	72·56	72·205	71·6
3HO	27·0	27·44	27·795	28·4
3HO, cPO^5	98·4	100·00	100·000	100·0

At 149°, the acid does not lose any water; at 160° it parts with its water very slowly. Evaporated in a platinum vessel to 213°, till it loses scarcely any more water, it still retains 23·02 per cent. (about $2\frac{1}{2}$ at.), and is for the most part converted into pyrophosphoric acid; for when

dissolved in water and mixed with soda, it yields abundance of crystals of pyrophosphate of soda, and but few of the ordinary phosphate. A small quantity of metaphosphoric acid is also formed even before the quantity of water has been reduced, by increase of heat, below 21·91 per cent. (2 at.); the quantity of this acid formed becomes considerable, if by raising the temperature above the melting-point of lead, the quantity of water is reduced below 18·7 per cent. (Graham.) When phosphoric acid is ignited in an open crucible, a considerable quantity of the acid volatilizes with the water; in a covered crucible this does not take place. After gentle ignition, the acid forms, on cooling, a soft glass containing about 20 per cent. of water; after stronger ignition, it forms a hard glass (metaphosphoric acid containing 10 per cent. of water). (Berzelius, *Lehrb.* 2, 64.) In an open platinum dish, pure hydrate of phosphoric acid may be completely evaporated. (H. Rose.)

Solution of ordinary Phosphoric acid.—Preparation. 1. From Phosphorus. *a.* Considerable quantities of phosphorus are burnt by degrees under a glass bell-jar, according to the method of Berzelius and Brunner (p. 123); the phosphoric acid washed together with water; the solution mixed with nitric acid and evaporated, in order to convert phosphoric oxide and phosphorous acid into phosphoric acid; and the excess of nitric acid removed by further evaporation. Or, according to Funke, phosphorus is burnt on a spoon in an oil of vitriol bottle containing a small quantity of water and nitric acid, and the solution evaporated. Leube (*J. pr. Chem.* 2, 276) decomposes the nitric acid by boiling with charcoal, till nitric oxide gas is no longer evolved; by this process, however, a quantity of artificial tannin may be introduced into the acid. The acid produced by the combustion is the metaphosphoric; but this when boiled is converted into the ordinary acid.

b. Phosphorus is converted by slow combustion (p. 120) into phosphatic acid; this is mixed boiling with nitric acid, as long as nitric oxide gas is evolved, and the excess of acid removed by evaporation. (Bucholz, *Beitr. zur Erweiterung d. Chem.* 1, 69.)

c. Phosphorus is heated with dilute nitric acid, by which it is dissolved, with evolution of nitric oxide gas, partly as phosphorous, partly as phosphoric acid; the liquid is evaporated—whereupon, at a certain degree of concentration, the nitric acid still present converts the phosphorous acid into phosphoric; more nitric is then added, till the evolution of nitric oxide gas ceases; and the evaporation is continued till all the undecomposed nitric acid is driven off.

The solution of the phosphorus in nitric acid is performed in a glass flask, or better in a retort, in order that the nitric and hyponitric acids, which carry phosphorus over with them (according to Wittstock, because phosphuretted hydrogen is evolved), may be collected in a receiver and poured back again. The solution is evaporated in basins of porcelain (the glazing of which is less easily attacked by the concentrated acid than glass) or of platinum. In concentrated nitric acid, phosphorus often takes fire; consequently, when strong acid is used, the phosphorus must be introduced in separate pieces, each being left to dissolve before another is put in. On this account, an acid of specific gravity 1·1 or 1·2 is to be preferred; the phosphorus may then be put in all at once without danger; if the effervescence should become too violent, the fire must be removed. One part of phosphorus requires about 13 parts of nitric acid of specific gravity 1·2, to dissolve it. (Wittstock.) The conversion of the phosphorous acid into phosphoric acid, and the effervescence attending

it, take place when the quantity of liquid is reduced to about eight times that of the phosphorus used. (Wittstock.) As soon as the effervescence begins, the liquid turns yellow (from the presence of hyponitric acid?). (Schönbein.) When the effervescence stops, nitric acid is added in small portions at a time, the heating being still continued as long as any effervescence is produced. Lastly, when the liquid is so far evaporated that its temperature rises to 188° (370° F.), in which case it weighs about four times as much as the original quantity of phosphorus, the whole of the nitric acid is expelled. (Wittstock.) If by very great concentration, bPO^5 or aPO^5 should be produced, these acids may be reconverted into cPO^5 by subsequent solution in water, and boiling*. If the phosphorus contains arsenic, this metal dissolves at first in the nitric acid, in the form of arsenious acid. This acid remains dissolved during the evaporation, provided there is sufficient nitric acid present to oxidate the phosphorous acid. But if this is not the case, and the remaining phosphorous acid evolves phosphuretted hydrogen gas, the arsenic is thereby reduced in the form of a black powder, which, on the addition of nitric acid, is re-dissolved with evolution of nitric oxide gas. The arsenic may therefore be removed by diluting and filtering the liquid from which it has separated, boiling down again, and treating the residue several times with phosphatic acid, till no more black powder separates. (Liebig.) Since, however, in this process, a great deal of phosphorus is lost in the form of phosphuretted hydrogen, Wittstock thinks it preferable to dissolve the phosphoric acid in water, after it has been completely oxidized by nitric acid, and freed from the excess of that acid by strong concentration—then saturate it with hydrosulphuric acid, and leave it to stand for some time. The excess of nitric acid, however, converts the arsenious into arsenic acid, which is but slowly precipitated by hydrosulphuric acid. The liquid must therefore be saturated with hydrosulphuric acid, placed for some days in a stoppered bottle, and if it then no longer smells of hydrosulphuric acid, again saturated, and put aside, &c.—till, even after several days, no more sulphide of arsenic is precipitated, and the liquid retains the odour of hydrosulphuric acid; it is then to be filtered, and freed by evaporation from hydrosulphuric acid. Warming the liquid while impregnated with hydrosulphuric acid, accelerates the precipitation, but, according to Bärwald, induces the formation of hyposulphuric acid (?). The acid thus prepared is free from ammonia. (L. A. Buchner.—*Comp.* Martins & Kastner, *Repert.* 15, 73; Bärwald, *Berl. Jahrb.* 33, 2, 113; Wittstock, *Berl. Jahrb.* 33, 2, 125; Liebig, *Ann. Pharm.* 11, 260; Schönbein, *J. pr. Chem.* 16, 121; L. A. Buchner, *Repert.* 66, 215; Gieseler, *N. Br. Arch.* 19, 313; Reinsch, *J. pr. Chem.* 28, 235.)

2. *From Bone-ash.* The bones of oxen burnt to whiteness contain, according to Berzelius, in 100 parts, 86 phosphate of lime, 6 carbonate of lime, 5 fluoride of calcium, and 3 phosphate of magnesia; other kinds of bone-ash are similarly composed.—(*a.*) 100 parts of bone-ash are digested with about 96 parts of oil of vitriol diluted with from 10 to 16 times its

* Reinsch has observed that phosphorus is but slightly attacked by nitric acid in an open vessel, and at comparatively low temperatures, because it becomes covered with a film of oxide. When the air is excluded and the temperature kept low, pure nitric oxide is evolved and phosphoric acid formed, the liquid acquiring a blue colour. At a boiling heat and out of contact of air, nitric acid acts upon phosphorus in such a manner that nearly all the oxygen of the liberated nitric oxide is transferred to the phosphorus, and nitrogen gas is evolved. If the air has access to the liquid, the nitric oxide is not decomposed (*J. pr. Chem.* 28, 385; *Ann. Pharm.* 48, 205). [W.]

weight of water; the phosphoric acid is strained through linen; the sulphate of lime remaining on the filter washed with water; and the liquid thus obtained is concentrated by evaporation, freed by filtration through linen from the sulphate of lime which separates from it, and further purified in various ways.

The oil of vitriol must be free from arsenious acid; otherwise this acid will be transferred to the phosphoric acid. The digestion of the bone-ash with the dilute sulphuric acid, which is performed with frequent stirring in vessels of porcelain, stoneware, or lead, must be continued for a day or more, the liquid being ultimately raised to the boiling point. Burnt bones in the solid state may also be used: the decomposition is complete when they are reduced to a paste. When the quantity of sulphuric acid is too small, phosphate of lime remains dissolved in the phosphoric acid: in this case, a further addition of sulphuric acid to the concentrated liquid precipitates sulphate of lime, which is almost insoluble in the liquid supersaturated with sulphuric acid. The excess of sulphuric acid may be removed by further evaporation; but sulphate of magnesia—which, on the application of a stronger heat, parts with its sulphuric acid and is converted into phosphate—and a small quantity of sesqui-oxide of iron, still remain mixed with the phosphoric acid. When 100 parts of bone-ash are digested in 90 parts of oil of vitriol, a portion of the phosphate of lime remains undecomposed: when equal weights are used, a small quantity of sulphuric acid remains in excess. (Funcke, *N. Tr.* 8, 2, 3.) Liebig (*Ann. Pharm.* 9, 255; 11, 260) employs equal parts of bone-ash and oil of vitriol—separates the phosphoric acid from the gypsum—concentrates it considerably—adds oil of vitriol to it when cool, as long as sulphate of lime separates—strains the liquid through linen, after diluting it with water—evaporates again—once more adds oil of vitriol as long as any precipitate is produced—and lastly, frees the filtrate from excess of sulphuric acid, by evaporating till the heat rises to redness. The residue is free from lime and sulphuric acid, but still contains magnesia, which can only be removed by solution in alcohol or by precipitation with carbonate of ammonia.

To purify phosphoric acid obtained from bone-ash by the action of sulphuric acid, as completely as possible from lime or magnesia, alcohol or ammonia may be used. *Purification by alcohol:* The acid evaporated to a syrupy consistence is agitated with excess of alcohol and filtered from the insoluble matter, which consists of lime and magnesia combined with phosphoric or sulphuric acid (any arsenious acid which may happen to be present remains dissolved, *Wackenroder*). The alcohol is recovered by distillation. In this process, small quantities of sulphovinic and phosphovinic acids are formed (Büchner, Liebig, *Ann. Pharm.* 9, 254), in consequence of which, the acid becomes yellow on further evaporation, and evolves olefiant gas. By igniting the acid these compounds are destroyed, the decomposition being attended with a blackening of the acid, which may be removed by nitric or sulphuric acid. Commercial phosphoric acid obtained from bones may also be dissolved in alcohol with addition of sulphuric acid; or again, the digested mixture of bone-ash and sulphuric acid may be at once exhausted with alcohol. (*Vid.* Trommsdorff, *N. Tr.* 1, 1, 51; 2, 1, 354; Trommsdorff, junr., *N. Br. Arch.* 11, 229.)

Purification by Ammonia. The liquid obtained by the decomposition of bone-ash by dilute sulphuric acid is saturated, after filtration, with carbonate of ammonia, which precipitates triphosphate of lime and am-

monio-phosphate of magnesia; the complete separation of the precipitate is facilitated by warming the liquid. The phosphate of ammonia obtained by evaporation of the filtrate is freed from ammonia by continued fusion at a red heat in a porcelain or platinum crucible. The residue is the hydrate of metaphosphoric acid, and must be reconverted into ordinary phosphoric acid by solution in water and boiling. But according to Dulong (*Mém. d'Arcueil*, 3, 444) and Balard (*Ann. Chim. Phys.* 57, 278), the whole of the ammonia is not expelled by a red heat, even when long continued; and at a white heat, phosphide of platinum is formed. Moreover, when porcelain crucibles are used, their glazing is strongly attacked by the acid, which thence becomes contaminated with alkali and earthy matters; and if crucibles of platinum are employed, the utmost care must be taken to ensure the absence of carbon, and consequently of all organic matters; since otherwise phosphorus will be reduced and will combine with the platinum, forming an easily fusible phosphide of the metal, and consequently the crucible will be perforated.

¶ *Gregory's Method of Purification.* The solution of phosphoric acid from which the lime has been separated by excess of sulphuric acid (Liebig's method), is evaporated to a syrup and gently ignited, to drive off the sulphuric acid. The glass thus obtained is dissolved in boiling water, and the solution, which is perfectly clear, concentrated by evaporation and maintained for a quarter or half an hour at a temperature of about 315° C. (600° F.), at which the phosphoric acid begins to evaporate with the water. A white powder then separates in considerable quantity, consisting, according to Gregory's analysis, of phosphoric acid and magnesia, in the proportion of 3 atoms of acid to 2 of base. The syrupy mass is left to cool, afterwards digested in cold water, and the liquid filtered. The filtrate is a solution of pure phosphoric acid. This method is much more advantageous than either of the preceding: for the glacial acid purified by alcohol still retains a considerable quantity of magnesia; and the mode of purification by ammonia is objectionable, on account of the difficulty of expelling the last traces of ammonia, and the great chance of injury to the platinum vessels. (Gregory, *Ann. Pharm.* 54, 94.) Maddrell, however, finds that the acid obtained by Gregory's process is not absolutely pure, but retains traces of magnesia and soda. The presence of soda in phosphoric acid obtained from bones appears to have been previously overlooked; it is of course derived from the bones themselves. Maddrell finds that the white precipitate above mentioned, which Gregory supposed to be an anomalous phosphate of magnesia, contains about 8 per cent. of soda, and is in fact a double metaphosphate of soda and magnesia: $3(MgO, PO^5) + NaO, PO^5$. (*Ann. Pharm.* 61, 53.) From these considerations it would appear that phosphoric acid quite free from the impurities above mentioned, can only be obtained either by dissolving phosphorus in nitric acid, or else by the method of Berzelius next to be described. But the acid obtained by Gregory's process appears to be sufficiently pure for nearly all purposes. ¶

b. Bone-ash is dissolved in the smallest possible quantity of nitric acid—the solution mixed, while still hot, with acetate of lead—and the precipitated phosphate of lead digested for some hours with the liquid, which possibly contains more or less acetate of lead in excess, in order to decompose the small quantity of phosphate of lime mechanically carried down with the precipitate. The phosphate of lead is then thoroughly washed on the filter with hot water, and afterwards dried and ignited, to destroy any organic matter which may be present. Finally, 100 parts of

the phosphate of lead thus obtained are decomposed by digestion with 33·25 parts of oil of vitriol and 400 of water—the liquid is filtered and evaporated—the sulphuric acid driven off by ignition in a platinum crucible—the residue dissolved in water—and the oxide of lead precipitated by hydrosulphuric acid gas. (Berzelius, *Lehrb.* 2, 61.)

Impurities in Phosphoric acid.—*Phosphorous acid:* Precipitates calomel from a solution of corrosive sublimate; produces a blackish, instead of a yellowish white precipitate with subnitrate of mercury; precipitates sulphur when heated with sulphurous acid; and evolves phosphuretted hydrogen gas when heated with dilute sulphuric acid in Marsh's apparatus (vide *Arsenic*).—*Metaphosphoric acid:* Gives with nitrate of baryta or nitrate of silver a white precipitate soluble in nitric acid.—*Sulphuric acid:* Gives with salts of baryta a white precipitate insoluble in hydrochloric acid.—*Nitric acid:* Decolorizes solution of indigo when heated with it; evolves nitric oxide gas when heated with copper or mercury; yields nitrate of lime when supersaturated with lime, filtered, and evaporated. [When the solution is mixed in a test-tube with sulphuric acid, and a solution of protosulphate of iron carefully poured upon it, a brownish-black ring is produced at the surface of separation of the two liquids. (W.)]—*Ammonia:* Evolved on supersaturating the liquid with lime or potassa.—*Lime:* Precipitated by ammonia; if, however, metaphosphoric acid be present, the mixture remains clear, because metaphosphate of lime is soluble in metaphosphate of ammonia, but becomes opalescent after some days, in proportion as cPO^5 is formed (Liebig); oxalic acid, however, precipitates the lime from the mixture.—*Magnesia:* Precipitated by ammonia, especially on the application of heat.—*Arsenious acid:* Immediate yellow precipitate by hydrosulphuric acid.—*Arsenic acid:* The liquid saturated with hydrosulphuric acid and kept in a stoppered bottle, deposits a yellow precipitate after a day or more; if the liquid has been boiled with sulphurous acid, the precipitate appears immediately. The presence of arsenious or arsenic acid may also be shown by Marsh's apparatus.—*Sesqui-oxide of iron:* Reddens sulphocyanide of potassium.—*Oxide of lead, or oxide of copper:* Precipitated black-brown by hydrosulphuric acid, after proper dilution of the liquid. (The statement of Runzler (*Br. Arch.* 3, 208), that lead is not precipitated from phosphoric acid by hydrosulphuric acid, is without foundation.)

The aqueous solution of phosphoric acid is of a syrupy consistence when concentrated. According to Dalton, 100 parts of this solution, of specific gravity 1·85, contain 50 parts of acid; at 1·6 sp. gr., 40 parts; at 1·39 sp. gr., 30 parts; at 1·23 sp. gr., 20 parts; and at 1·1 sp. gr., 10 parts of acid. It gives a white precipitate with baryta, strontia, or lime-water, and with solution of acetate of lead; does not precipitate chloride of barium or strontium, or white of egg; and gives with nitrate of silver, on the addition of a small quantity of ammonia, a precipitate of a bright yellow colour.

b. Combinations with Salifiable Bases: *Phosphates in general.* The affinity of phosphoric acid for bases is greater than that of carbonic, boracic, hypophosphorous, or phosphorous acid, and it neutralizes the bases more completely. Phosphates are fixed in the fire, provided the base be so, and for the most part, easily fuse to a vitreous mass. Charcoal appears not to decompose the compounds of phosphoric acid with the fixed alkalis, even at a strong red heat, excepting when silica is

present. (II., 104.) Of the remaining salts of phosphoric acid, some are resolved by charcoal into metallic oxide and free phosphorus (magnesia); some into metal and free phosphorus (oxide of lead); others are converted into metallic phosphides, part of the phosphorus, however, being at the same time set free. If a salt of phosphoric acid be fused with boracic acid on charcoal before the blowpipe, and when the glass has been brought to a state of tranquil fusion, a small piece of fine harpsichord wire be put into it, and the inner flame directed upon it with a strong blast, a fused globule of brittle magnetic phosphide of iron will be formed. If the base of the salt is such as would exert a disturbing action, the salt may be dissolved in hydrochloric acid, the solution saturated when cold with hydrated sesqui-oxide of iron, the filtrate heated to the boiling point, and the basic phosphate of iron thereby precipitated, treated as above with boracic acid and harpsichord wire. (Berzelius.)

Phosphates heated with potassium yield phosphide of potassium. If, therefore, a phosphate be heated with potassium in a glass tube, and, when the mass has cooled, the excess of potassium be removed by mercury, and moist air blown in, or if the residue be moistened with water—phosphuretted hydrogen gas, easily detected by its odour, is evolved. (Thénard; Vauquelin.)

All phosphates are decomposed by sulphuric acid. A platinum wire moistened with oil of vitriol, then dipped in the finely-pounded salt, and heated in the blowpipe flame, imparts to it a green colour easily recognizable in the dark. (Fuchs, Erdmann, *Schw.*, 24, 130; 59, 26.)

The compounds of phosphoric acid with potassa, soda, and lithia are soluble in water, in whatever proportions the base and acid may be united. The remaining phosphates are nearly insoluble in water excepting when they contain an excess of phosphoric acid. They are likewise all soluble in dilute nitric acid. The solutions give with nitrate or acetate of lead a white pulverulent precipitate of phosphate of lead. This precipitate, when heated upon charcoal in the outer blowpipe flame, fuses to a globule which, on cooling, solidifies to an angular mass; with borax it forms a glass which is transparent while hot, but becomes opaque and white upon cooling; when very strongly ignited upon charcoal, it evolves phosphorus; diffused through water and decomposed by hydrosulphuric acid, it yields a filtrate containing phosphoric acid. Of the insoluble phosphates, some do not give up any of their acid to fused hydrate of potassas or boiling solution of potassa (*e. g.* triphosphate of lime); others give up nearly all, (*e. g.* the phosphates of magnesia, protoxide of cerium, sesqui-oxide of chromium, protoxide of manganese, sesqui-oxide of iron, and protoxide of nickel).

Metaphosphates. These salts are produced when aqueous metaphosphoric acid is brought in contact with a base, or when one atom of pyrophosphoric, or of ordinary phosphoric acid is ignited with one atom of base. They always contain one atom of base and one atom of acid; *e. g.* NaO, aPO^5. The soluble salts have a slight acid reaction; they precipitate chloride of barium in gelatinous flakes, and the salts of many earths and heavy metallic oxides in the form of liquid hydrates; these precipitates likewise become more or less fluid on boiling the liquid. When the solution is very dilute, only a slimy precipitation is produced. The metaphosphates give a white precipitate with nitrate of silver. That obtained with baryta is converted, by boiling for several hours, into 3BaO, cPO^5. (Graham.)

¶ *Modifications of Metaphosphoric acid.* The metaphosphates just spoken of, are those which are formed by double decomposition from the vitreous metaphosphate of soda, obtained by quickly cooling the salt from a state of fusion. They are wholly destitute of crystalline structure, and it is difficult to obtain them in a definite form. The vitreous metaphosphate of soda may, however, be brought into the crystalline state by very slow cooling. If a considerable quantity of the vitreous salt be fused in a platinum crucible enclosed within one or more earthen crucibles, and left to cool very slowly, the mass when solidified is found to have acquired a beautiful crystalline structure; and on digesting this crystalline mass in warm water, not using a very large excess, the liquid divides into two strata, the one which is the larger in quantity containing the crystallized metaphosphate, and the other the common vitreous salt. When the solution of the crystallized salt is mixed with solutions of various metallic oxides, *e. g.* nitrate of silver, acetate of lead, chloride of barium, &c., crystalline salts of the various bases are obtained, containing water of crystallization: *e. g.* $3(AgO, PO^5) + 2HO$; $PbO, PO^5 + HO$, &c. (Fleitmann & Henneberg, *Ann. Pharm.* 68, 304.) By adding dilute phosphoric acid in excess to solutions of various metallic salts, evaporating to expel excess of acid, and heating to upwards of 316° C. (600° F.), metaphosphates of the various bases are produced in the form of earthy powders, which are all, even the potassa and soda salts, insoluble or nearly so in water. (Maddrell, *Mem. Chem. Soc.* 3, 373.) It appears then that metaphosphoric acid—at least in combination with salifiable bases—is susceptible of three distinct modifications. These are attributed by Messrs. Fleitmann & Henneberg to polymeric conditions: thus, the three classes of salts may perhaps be represented by MO, PO^5; $2MO, 2PO^5$; $3MO, 3PO^5$; or possibly by MO, PO^5; $3MO, 3PO^5$; $6MO, 6PO^5$. ¶

Pyrophosphates. These salts are formed when aqueous pyrophosphoric acid is brought in contact with a salifiable base, or when one atom of metaphosphoric or ordinary phosphoric acid is ignited with two atoms of base. They contain either 2 atoms of base to 1 atom of acid, *e. g.* $2NaO, bPO^5$: *Normal* or *Di-pyrophosphates;* or 1 atom of base and 1 atom of water to 1 atom of acid, *e. g.* NaO, HO, bPO^5: *Acid* or *Simple Pyrophosphates.* The soluble normal salts have a slight alkaline reaction. Both the normal and the acid soluble salts give white precipitates with chloride of barium and nitrate of silver, the latter precipitate forming a chalky powder. When a quantity of dipyrophosphate of soda ($2NaO, bPO^5$) containing 1 part of phosphoric acid is dissolved in 10,000 parts of water, the solution produces a strong turbidity in baryta or lime-water, and in solutions of nitrate of baryta, chloride of calcium, and nitrate of silver; with 20,000 parts of water, the turbidity is faint; with 40,000 parts very faint, not appearing for half-an-hour in lime-solutions; with 80,000 parts of water, the lime-solutions give no turbidity, and the other three, only a very faint cloudiness; and with 160,000 parts of water, the same solutions produce nothing more than a faint opalescence. (Lassaigne, *J. Chim. Med.* 8, 523.)

Ordinary Phosphates. These are produced on bringing ordinary phosphoric acid in contact with a base, and on igniting one atom of metaphosphoric or pyrophosphoric acid with 3 or more atoms of base. For 1 atom of acid they contain, either 3 atoms of base: *Normal* or *Tri-phosphates,* otherwise called *Basic, e. g.* $3NaO, cPO^5$; or 2 atoms of base and 1 atom of basic water: *Di-phosphates,* otherwise called *Neutral, e. g.* $2NaO, HO, cPO^5$, the ordinary phosphate of soda; or 1 atom of base

and 2 atoms of basic water: *Simple Phosphates*, otherwise called *Acid, e. g.* $NaO, 2HO, cPO^5$. The bibasic salts sometimes contain two different bases with one atom of water, *e. g.* NH^4O, NaO, HO, cPO^5. The tribasic alkaline phosphates have a strong, the bibasic a weak alkaline reaction, while the simple salts have an acid reaction. The tribasic salts suffer no change by ignition; the bibasic salts are thereby converted into pyrophosphates, inasmuch as 1 atom of water is driven off, and there remain 2 atoms of base united to 1 atom of acid, *e. g.* $2NaO, HO, cPO^5$ is converted into $2NaO, bPO^5$; and the simple phosphates are changed into metaphosphates, since 2 atoms of basic water are evolved, and there remains but 1 atom of base united with 1 atom of acid, *e. g.* $NaO, 2HO, cPO^5$ becomes NaO, aPO^5. (Graham.) All soluble ordinary phosphates give white precipitates with a mixture of a salt of magnesia, sal-ammoniac, and ammonia; white with lead-salts, and lemon-yellow with nitrate of silver; the tribasic and bibasic, but not the simple salts, precipitate chloride of barium. Ordinary phosphates precipitate baryta-water and lime-water. Those which are not soluble in water dissolve easily in nitric acid; acetic acid dissolves most of them, though less easily, and the lead-salt and the salt of ferric oxide not at all. They are also slightly soluble in ammoniacal salts, especially in sal-ammoniac. Ammonia precipitates them, both from solution in acids, and likewise, for the most part, from their solutions in ammoniacal salts. The solution of ordinary phosphates in nitric acid, likewise, when it does not contain too great an excess of acid, precipitates lead-salts white, and silver-salts lemon-yellow; and the precipitates increase in quantity when ammonia is carefully added so as not completely to neutralize the acid.

¶ *Phosphates of the form* $3MO + 2PO^5$. Phosphates of this form have lately been discovered by Fleitmann & Henneberg. The soda-salt is obtained by fusing together 76·87 parts of metaphosphate (the vitreous metaphosphate to which the name was originally applied) and 100 parts of anhydrous pyrophosphate of soda, or 187·27 metaphosphate to 100 parts of the salt $3NaO, PO^5$. The materials are very intimately mixed by pounding in a mortar, and then fused in a platinum crucible, the mass being kept for some time in the liquid state and continually stirred. The salt when cool is finely pounded and digested in a quantity of hot water, not quite sufficient to dissolve it: an excess would decompose it. The solution, after filtering, is left to evaporate over sulphuric acid. By this process, the salt is obtained in the form of a white crystalline mass. It is soluble in about 2 parts of cold water, the solution having a weak alkaline reaction. From this salt, other phosphates of similar constitution may be obtained by double decomposition, *e. g.* $3AgO, 2PO^5$; $3MgO, 2PO^5$; $3BaO, 2PO^5$, &c.

Phosphates of the form $6MO, 5PO^5$. This group of salts has likewise been discovered by Fleitmann & Henneberg. The soda-salt is obtained by fusing together 100 parts of pyrophosphate of soda and 307·5 of metaphosphate. It is very unstable, more so than the last. It may, however, be obtained in the crystalline form. After fusion, it forms a vitreous mass, like metaphosphate of soda. The silver-salt, $6AgO, 5PO^5$, is obtained by double decomposition: it is easily soluble in excess of the soda-salt.

The two classes of salts just described are intermediate between the metaphosphates and the pyrophosphates. If we suppose that in all salts of phosphoric acid the acid is united with 6 atoms of base,

the whole family will be represented by the following continuous series.

Common Phosphate	$6MO, 2PO^5$
Pyrophosphate	$6MO, 3PO^5$
Fleitmann & Henneberg's new Phosphates	$6MO, 4PO^5$ $6MO, 5PO^5$
Metaphosphate	$6MO, 6PO^5$

(*Ann. Pharm.* 65, 304.) ¶

Phosphorus and Hydrogen.

A. Protophosphide of Hydrogen?

a. The yellow powder which, according to H. Rose (*Pogg.* 12, 549), separates during the decomposition of phosphide of potassium by water, enters into fusion at a temperature at which phosphorus sublimes, and at the same time evolves hydrogen gas. (Magnus, *Pogg.* 17, 527.)

b. 1. Phosphuretted hydrogen gas obtained by moderately heating phosphorus with milk of lime, collected over water which has been well boiled and is still warm, and exposed to strong daylight in bottles having their necks immersed in water, deposits yellow flakes, which, when they no longer increase in quantity and the gas has lost its spontaneous inflammability, may be collected, freed from water by decantation, and dried at 50°. If the gas is exposed to direct sunshine, the yellow colour of the flakes is less brilliant. 2. When a mixture of equal measures of chlorine and carbonic acid gases is passed into excess of phosphuretted hydrogen, the same deposit is produced, but so finely divided that it cannot be collected: pure chlorine produces too high a temperature, and consequently separates pure phosphorus.

Greenish-yellow flakes, heavier than water, smelling like phosphorus, tasteless. From the mean of several experiments, this substance appears to be PH. Heated in a stream of carbonic acid gas to a temperature above 175°, it is resolved into hydrogen gas and phosphorus. Exposed under boiled water to the solar rays, it gradually disappears, decomposing the water with evolution of hydrogen gas and formation of acid. It takes fire in the air at temperatures between 140° and 150°, according as it is more or less finely divided. A drop of strong sulphuric acid sets it on fire immediately, producing a long flame. It dissolves in dilute nitric acid at temperatures between 30° and 40°. With chlorine, it forms chloride of phosphorus and hydrochloric acid. It is decomposed by copper and silver salts. It is insoluble both in water and in alcohol. (Leverrier, *Ann. Chim. Phys.* 60, 175.)

¶ According to Paul Thénard (*N. Ann. Chim. Phys.* 14, 5), this substance is composed of two atoms of phosphorus and one of hydrogen, or in 100 parts, 98·43 P + 1·57 H. It may be obtained in a state of purity by the action of strong hydrochloric acid on phosphide of calcium, PCa^2, phosphuretted hydrogen gas being produced at the same time.

$$5PCa^2 + 10HCl = 10\,CaCl + P^2H + 3PH^3.$$

It is probable, however, that the liquid phosphide, PH^2, is first produced (*vid.* p. 148), and immediately resolved by the excess of acid into solid

phosphide and phosphuretted hydrogen gas. As soon as the evolution of phosphuretted hydrogen is at an end, the insoluble residue is to be washed and afterwards dried in vacuo. Solid phosphide of hydrogen may also be obtained by passing spontaneously inflammable phosphuretted hydrogen gas through concentrated hydrochloric acid, care being taken to prevent the stoppage of the tube.

This substance is yellow when freshly prepared, but becomes orange-coloured by exposure to light; it is inodorous; takes fire at 200°, also when struck on the anvil by a hammer; it is not altered by dry air at ordinary temperatures, slowly by damp air. Heated in hydrogen gas, it distils and is decomposed, yielding phosphuretted hydrogen gas. It first assumes an orange-red colour; then, at a higher temperature, phosphorus distils over; the colour becomes dark grey; and, after a further application of heat, the substance disappears entirely. The only liquid which dissolves it without decomposition is the liquid phosphide of hydrogen. Chlorine, perchloride of phosphorus, and sulphuric acid decompose it instantly. Solution of caustic potassa in absolute alcohol dissolves it with evolution of phosphuretted hydrogen gas mixed with more or less free hydrogen, and there remains a red liquid which quickly changes: this, after a few hours, becomes colourless, hydrogen is evolved, and hyposulphite of potassa deposited. On the application of heat, the decomposition is immediate. Water added to the red liquid produces a dirty-yellow precipitate; acids, a greenish-yellow precipitate of phosphoric oxide. Solid phosphide of hydrogen added to solution of sulphate of copper, produces phosphide of copper mixed with metallic copper. With chlorate of potassa it detonates violently when struck or heated; less violently with oxide of silver or mercuric oxide. With oxide of copper it detonates when heated, and often with great violence. Hence all experiments with this substance must be conducted with great caution.

The greenish residue obtained in the preparation of spontaneously inflammable phosphuretted hydrogen by heating phosphorus with milk of lime, or by the action of water on phosphide of calcium, appears, according to Thénard's observations, to be isomeric with the preceding. It is decomposed by heat. Like the yellow phosphide, it is completely dissolved, with evolution of phosphuretted hydrogen gas, by alcoholic solution of potassa; the solution is blood-red. It is not altered by boiling with hydrochloric acid. ¶

B. Phosphuretted Hydrogen Gas. PH^3.

Phosphorwasserstoff-gas, Phosphorluft, phosphorhaltiges, gephosphortes Wasserstoff-gas, Gas hydrogène phosphoré, Gas hydrogenium phosphoratum. This gas appears sometimes to occur in nature as the cause of *Ignes Fatui* and similar luminous appearances.

Phosphuretted hydrogen gas occurs in two different states:

1. *Spontaneously inflammable Phosphuretted Hydrogen:* takes fire in the air at ordinary temperatures, and under the ordinary atmospheric pressure.

2. *Non-spontaneously inflammable Phosphuretted Hydrogen:* takes fire only at elevated temperatures, or under diminished pressure.

Formation. This compound is produced when phosphorus and hydrogen come in contact at the moment of separation from other combinations, that is to say, in the nascent state. If the hydrogen has once assumed

the gaseous state, it is no longer capable of entering into this combination. When phosphorus is kept for some time in a state of fusion in hydrogen gas, vapour of phosphorus diffuses itself through the gas, imparting to it the odour of garlic and the property of emitting light in contact with oxygen gas; without, however, the occurrence of an actual chemical combination between the phosphorus and hydrogen. (Fourcroy & Vauquelin, *Ann. Chim.* 21, 202.)

Formation of the more inflammable gas. 1. The compounds of phosphorus with the alkali-metals are resolved, by contact with water, into an alkaline hypophosphite and phosphuretted hydrogen.—2. Phosphide of zinc, tin, or iron, with aqueous sulphuric or hydrochloric acid, yields a metallic sulphate or chloride and phosphuretted hydrogen gas. Zinc exposed in contact with granulated phosphorus to the action of dilute sulphuric acid, evolves, not phosphuretted hydrogen as stated by Davy, but pure hydrogen gas, with which, when the acid is heated, vapour of phosphorus becomes mixed. (Dumas, *Ann. Chim. Phys.* 31, 135.)—3. Phosphorus heated in an aqueous solution of a fixed alkali, yields phosphuretted hydrogen gas together with a hypophosphite and phosphate of the alkali. Such an action is exerted by potassa, soda, lithia, baryta, strontia, and lime, and, according to Raymond, by oxide of zinc and protoxide of iron. Potassa causes an evolution of gas even at 15°. The affinity of phosphorus for hydrogen + that of phosphorus for oxygen + the predisposing affinity of the alkali for phosphoric and hypophosphorous acid, overcomes the powerful affinity between hydrogen and oxygen. From the very beginning of the action, the phosphuretted hydrogen gas is mixed with more or less free hydrogen, and there is likewise a certain quantity of phosphate produced; but as the boiling is continued and the solution becomes more concentrated, the quantity of hydrogen gas continually increases; because a greater and greater quantity of the alkaline hypophosphite is resolved, together with water, into hydrogen gas and a phosphite of the alkali (II., 114). *H. Rose.*—4. When hypophosphites are heated, the phosphuretted hydrogen evolved is generally of the more inflammable, more rarely of the less inflammable variety, mixed with a certain quantity of vapour of phosphorus and free hydrogen gas. (H. Rose.)—5. In the putrefaction of organic bodies containing phosphorus: hence the odour of decayed fish.

Formation of the less inflammable gas. 1. When the hydrate of phosphorous acid (H. Davy), or of hypophosphorous acid is heated. (Dulong.)—2. When zinc or iron is dissolved in aqueous phosphorous acid (Berzelius), or zinc in a mixture of aqueous phosphorous acid and sulphuric acid. (Wöhler.)—3. When phosphorus is boiled with hydrate of potassa and alcohol, the non-inflammable gas is evolved mixed with hydrogen gas and alcohol vapour, and there remains hypophosphite of potassa and a small quantity of phosphate, together with excess of potassa. (H. Rose.) Grotthuss (*Ann. Chim.* 64, 32, also *M. Gehl.* 5, 608; further *Schw.* 32, 274), took this mixture for a peculiar gas, which he called *Phospho-carburetted Hydrogen.*—4. When phosphide of calcium is decomposed by concentrated hydrochloric acid. (Dumas.)—5. Phosphorus, under the influence of light, decomposes water, producing phosphoric oxide and phosphuretted hydrogen gas, which remains dissolved in the water.

A flask was completely filled with granulated phosphorus and water, and connected with a bent tube filled with water, the other end of the tube dipping under mercury. After six weeks' exposure to the rays of the summer sun, the following effects were produced. 1. The water in

the tube reddened litmus, gave a white precipitate with solution of corrosive sublimate, brown with solution of silver and brown-black after a time with solution of sulphate of copper, out of contact of air.—2. The flask was connected with a gas-delivery tube filled with water and heated to the boiling point. Phosphuretted hydrogen gas, equal in volume to about $\frac{1}{16}$ of that of the flask, was evolved together with the aqueous vapour. This gas was not spontaneously inflammable: solution of sulphate of copper absorbed about 90 per cent. of it, producing a brown-black precipitate. The water after thorough boiling exhibited, when rapidly filtered, the same reactions as the water out of the bent tube; but it no longer precipitated solution of sulphate of copper in a closed vessel completely filled with it. The phosphorous acid is probably accidental, inasmuch as the granulation of the phosphorus and the filling of the flask with water were performed during the heat of summer. It is remarkable that the filtered water of the flask diffused white fumes through the vessel, and smelt of phosphorus,—an effect which cannot be due to the small quantity of phosphorous acid present, but indicates a certain amount of solubility of the phosphorus in water. (Gm.) Phosphorus kept under water and exposed to light (in the dark the effect is produced less strongly and more slowly) imparts to the water a peculiar odour and the property of giving a dark-coloured precipitate with nitrate of silver or subnitrate of mercury; this latter property, however, is lost by exposure to the air. (Phillips, *Ann. Phil.* 21, 470.) Water in which phosphorus is immersed acquires a peculiar taste, a poisonous action, and the property of emitting light when mixed with hot water. (Murray, *Ann. Phil.* 16, 230.) When phosphorus is kept for some time under water in a well-stopped bottle, it emits light every time the vessel is shaken, and often gives a transient light even when no agitation takes place. On opening the bottle, this appearance ceases, and does not show itself again till the vessel has been kept well closed for some time. (Berzelius, *Lehrb.* 1, 222.) This luminosity disappears after several days, if the bottle be kept with the stopper turned downwards and shaken every day,—but reappears on opening it again for an instant: it appears to arise from the combustion of the phosphorus or phosphuretted hydrogen gas in very highly rarefied oxygen gas. (Gm.)

Preparation of the more inflammable gas. 1. By bringing phosphide of potassium, barium, or calcium in contact with water. Thomson fills a small tubulated retort three-fourths with thoroughly boiled water and one-fourth with nitric acid—introduces phosphide of calcium through the tubulure—fills the neck likewise with boiled water—and applies a gentle heat. One ounce of phosphide of calcium yields 70 cubic inches, and 16 grammes yield 1 litre of gas. Dumas causes water or very dilute hydrochloric acid to come in contact with phosphide of barium or phosphide of calcium placed at the top of a bell-jar filled with mercury. The gas obtained by means of phosphide of barium and water contains, according to Dumas, 43·2 measures in a hundred of free hydrogen gas; that obtained with phosphide of calcium and water contains 13; and when phosphide of calcium and dilute hydrochloric acid are the acting substances, the gas first evolved contains 7, and that last evolved 13 per cent. Buff likewise found between 13·5 and 14·5 per cent. of free hydrogen in the gas obtained by the mutual action of phosphide of calcium and water.

2. By heating phosphorus with aqueous solutions of the alkalis.—*a.* Gengembre boils 1 part of phosphorus with 2 parts of concentrated solution of potassa in a gas-generating vessel. H. Rose also recommends solution

of potassa concentrated as much as possible, and likewise that it be pure, since impurities produce frothing. The liquid is heated only so long as the gas is evolved without the application of a stronger heat; after that, the quantity of free hydrogen increases. (H. Rose.) The gas obtained always contains 62·5 measures per cent. of free hydrogen. (Dumas.) As the alkaline liquid only fills a small part of the vessel, the air which remains in it often produces explosions with the portions of gas first evolved,—whereby the vessel is burst, or at all events, the water is forced back into it. To prevent these explosions, the air is either deprived of part of its oxygen by the introduction of burning sulphur matches before the gas-delivery tube is adjusted in its place—by which means the violence of the explosions is diminished; or what is better—the bottle is only loosely covered with the stopper of the gas-delivery tube, when the heat is first applied (this is H. Rose's plan) and not closed air-tight till the gas which escapes near the stopper begins to burn with a brilliant flame. If the liquid together with the melted phosphorus should pass over, the phosphorus as it cools may stop up the tube and thereby cause the bottle to burst when the heating is continued.—*b.* Raymond heats in a gas-generating vessel one part of phosphorus with 16 parts of hydrate of lime and 4 parts of water (*Ann. Chim.* 10, 19). Dry hydrate of lime heated with phosphorus yields a gas containing a much larger quantity of free hydrogen than that prepared with solution of potassa. The quantity of free hydrogen increases considerably on further heating, by which the hypophosphite of lime is converted into phosphate. (H. Rose.) The gas evolved by heating phosphorus with milk of lime is found, when collected in 7 separate portions, to contain in 100 measures,—first 34 measures, then 27, then 39, then 44, then 50, then 60, then 86, and ultimately, when the vessel is heated nearly to redness, from 89 to 90 measures of free hydrogen gas. (Dumas.)

Preparation of the less inflammable gas. 1. By heating crystallized phosphorous acid in the gas-generating apparatus. (H. Davy.) Phosphatic acid may also be used for this purpose. The gas prepared in green glass retorts is pure, only the portions last evolved containing a little free hydrogen; but that which is prepared in white glass retorts contains hydrogen gas, because an alkaline phosphite is produced, with separation of silica,—and this when heated evolves hydrogen. (H. Rose.)—2. The same gas is evolved on heating hydrated hypophosphorous acid. (H. Rose; Dumas.) The first portions of gas evolved by methods 1 and 2 are perfectly pure; the latter portions deposit phosphorus (from the action of a greater degree of heat ?) and contain, in 100 measures, from 17 to 25 measures of free hydrogen. (Dumas.)—3. By decomposing phosphide of calcium by rather strong hydrochloric acid. Ten cubic centimetres of concentrated hydrochloric acid being placed over mercury in a glass jar, a gramme of phosphide of calcium pounded and wrapped up in paper is rapidly passed up the mercury before it has time to take fire. Decomposition ensues, with powerful development of heat and separation of phosphorus. The gas obtained is quite pure, or else contains not more than from 1 to 5 per cent. of free hydrogen. Hydrochloric acid diluted with an equal bulk of water likewise evolves a pure gas, with separation of phosphorus; but the decomposition is slower, because the development of heat is less. (Dumas.)

To detect the free hydrogen mixed with phosphuretted hydrogen, the gas is brought into contact with solution of chloride of lime (Dalton), or of sulphate of copper, corrosive sublimate, or nitrate of silver. (Dumas ;

H. Rose.) These bodies decompose phosphuretted hydrogen, but leave unchanged the free hydrogen which may be mixed with it.

Properties of the more inflammable and less inflammable gases. Colourless. Sp. gr. (I., 279.) The free hydrogen which is frequently mixed with the gas diminishes its specific gravity considerably; hence it was formerly given much lower. The gas smells like stinking fish: or more properly speaking,—the fish in a state of decomposition smell like the gas, since they evolve it. It is irrespirable, exerting a positively deleterious action. It does not support combustion, but takes fire in the air, sometimes spontaneously, sometimes when heated; has no action on vegetable colours.

	Calculation.		H. Rose.	Dumas. *a*	Dumas. *b*	H. Davy.	Leverrier.	Leverrier. *a*	Leverrier. *b*
P	31·4	91·28	91·32	94·12	91·51	83·3	91·36	91·63	91·31
3H	3	8·72	8·68	5·88	8·49	16·7	8·64	8·37	8·69
PH^3	34·4	100·00	100·00	100·00	100·00	100·0	100·00	100·00	100·00

	Volume.	Sp. gr.	Or:	Vol.	Sp. gr.
Vapour of phosphorus	1	4·3539		¼	1·0885
Hydrogen gas	6	0·4158		1½	0·1039
Phosphuretted Hydrogen Gas	4	4·7697		1	1·1924

(H^3P = 3 . 6·2398 + 196·14 = 214·86. Berzelius.)

The gas *a* examined by Dumas and Leverrier was spontaneously inflammable; the gas *b*, inflammable only when heated. According to these experimenters, the two gases are differently constituted, the spontaneously inflammable gas having, according to Dumas, the composition PH^2 or P^3H^6; 4 volumes of it contain 1½ measures of vapour of phosphorus, and 6 measures of hydrogen gas (*vid. seq.*).

Decompositions. The spontaneously inflammable gas exposed to light over mercury or well-boiled water deposits nothing, (unless vapour of phosphorus were previously mixed with it,) and remains unaltered. (H. Rose.) The less inflammable gas likewise remains unaltered. (Graham.)

1. When a succession of electric sparks is passed through the spontaneously inflammable gas, the phosphorus is deposited in the form of a red film, and the gas is converted into 1⅓ (properly 1½) times its volume of pure hydrogen. (Dalton.) The less inflammable gas when electrified (for a shorter time?), deposits phosphorus and becomes spontaneously inflammable. (Graham.)

2. *Rapid Combustion.* The spontaneously inflammable gas takes fire at ordinary temperatures and under ordinary pressures in contact with air or oxygen gas. Even when passed through a tube 7 feet long, and surrounded with a freezing mixture cold enough to solidify mercury, it takes fire on escaping into air of the temperature of −15° (−5° F.). (H. Rose.) The inflammation of single bubbles of the gas, as they escape into the air, is attended with a very vivid light and the formation of a thick, white, ring-shaped cloud of hydrated phosphoric acid. In oxygen gas the combustion is exceedingly brilliant, resembling flashes of lightning, and, when the quantity is large, attended with fracture of the vessel. When sufficient oxygen is present, the products of the combustion are phosphoric acid and water; but a small portion of the phosphorus is converted into phosphoric oxide, which is deposited on the water and on the vessels

in the form of a yellowish-red film. The less inflammable gas does not take fire in air or oxygen gas at ordinary temperatures, either under ordinary or increased atmospheric pressure; under ordinary pressure, it inflames at 149° (300° F.). (H. Davy.) At ordinary temperatures inflammation does not take place unless the gaseous mixture is rarefied. (Houton Labillardière.) A strong glass tube being surrounded with a piece of stout wire-gauze (because it is very liable to burst), and placed in a very inclined position over the mercurial trough, a mixture of oxygen and the less inflammable phosphuretted hydrogen is passed up into it; if it be then raised into the upright position, so as to expand the gaseous mixture by about 2 decimetres, explosion immediately takes place. (Houton Labillardière.) Explosion by alteration of level takes place with peculiar facility when there is an excess of phosphuretted hydrogen present; *e. g.* with 2 measures of the latter and 1 measure of oxygen; a mixture of 1 measure of phosphuretted hydrogen with $1\frac{1}{2}$ measures of oxygen scarcely ever takes fire on setting the tube upright, if the oxygen be introduced first. (Dumas.) If a mixture of 1 volume of the less inflammable gas and 3 volumes of oxygen be introduced into a tube standing over mercury, and already containing a small quantity of oxygen gas, no inflammation takes place; but if this effect be brought about by the application of heat, every bubble of the mixture which is brought in contact with the remaining oxygen after the tube has completely cooled, takes fire. (H. Rose.) The less inflammable gas mixed with air and kept over mercury at the ordinary pressure, invariably explodes after a few hours. (H. Rose.) When exploded with excess of air or oxygen gas, 1 volume of phosphuretted hydrogen gas, whether spontaneously inflammable or not, consumes 2 volumes of oxygen gas. According to page 140, 4 volumes of phosphuretted hydrogen gas contain 6 volumes of hydrogen, which consume 3 volumes of oxygen in order to form water, and 1 volume of vapour of phosphorus, which requires 5 volumes of oxygen to convert it into phosphoric acid. Or, 1 volume of phosphuretted hydrogen gas contains $1\frac{1}{2}$ vol. of hydrogen, which require $\frac{3}{4}$ vol. oxygen,—and $\frac{1}{4}$ vol. vapour of phosphorus, which requires $\frac{5}{4}$ vol. oxygen; and $\frac{3}{4} + \frac{5}{4} = 2$. The spontaneously inflammable gas introduced in bubbles into excess of oxygen, deposits part of its phosphorus in the form of a yellowish-red film, and then consumes a smaller quantity of oxygen. To obtain perfect combustion, Dumas mixes the spontaneously inflammable gas with an equal volume of carbonic acid, and similarly with the oxygen—brings the two gaseous mixtures in contact—and inflames the mixture by heating it to 120°. In this case, according to Dumas, 1 volume of the spontaneously inflammable gas consumes only 1·83 vol. oxygen; and he supposes, since the explosion is accompanied by only a feeble light, that phosphorous instead of phosphoric acid is produced,—a supposition which Rose justly regards as improbable. According to Buff also, 1 volume of spontaneously inflammable phosphuretted hydrogen mixed with 3 volumes of carbonic acid, and then with excess of oxygen, consumes 2 volumes of the latter when exploded. Also, according to Dalton's later assertion, 1 volume of the spontaneously inflammable gas consumes 2 volumes of oxygen. The less inflammable gas exploded with excess of oxygen, absorbs somewhat less than 2 volumes, because part of the phosphorus is precipitated unburnt. (H. Davy.) But according to Dumas, the quantity of oxygen consumed is exactly 2 volumes. When the quantity of oxygen in the mixture is insufficient for complete combustion, the phosphorus burns first, and pure hydrogen gas is left, its volume sometimes amounting to $\frac{1}{2}$ more than that

of the phosphuretted hydrogen. (H. Davy.) When a mixture of 1 volume of the less inflammable gas with $1\frac{1}{2}$ vol. oxygen is inflamed in a narrow tube by the electric spark, it is resolved, without deposition of phosphorus, into water and phosphorous acid, a small residue being left, consisting sometimes of hydrogen, sometimes of hydrogen and oxygen, sometimes of phosphuretted hydrogen: $1\frac{1}{2}$ vol. hydrogen gas requires $\frac{3}{4}$ vol. oxygen, and $\frac{1}{4}$ vol. vapour of phosphorus requires $\frac{3}{4}$ vol. oxygen to form phosphorous acid; and $\frac{3}{4} + \frac{3}{4} = 1\frac{1}{2}$. (Dumas.) A mixture of 2 volumes of phosphuretted hydrogen and 1 volume of oxygen, exploded by rarefaction, deposits a large quantity of phosphorus, and leaves a residue consisting of pure hydrogen and phosphuretted hydrogen. (Dumas.)

3. *Slow Combustion.* When spontaneously inflammable phosphuretted hydrogen gas and oxygen gas are brought together in a tube only 0·3 of an inch in diameter, no combustion takes place, because the sides of the tube exert a cooling action. (Dalton.) In this action, according to Thomson, one volume of phosphuretted hydrogen absorbs half a volume (more correctly $\frac{3}{4}$) of oxygen, and forms phosphorous acid, whilst one volume (or more correctly $1\frac{1}{2}$) of pure hydrogen remains. Both varieties of phosphuretted hydrogen gas, when kept over water containing air, undergo a similar slow combustion, and the more inflammable gas loses its spontaneous inflammability.

4. Phosphuretted hydrogen gas takes fire in chlorine gas at ordinary temperatures, burns with a brilliant greenish-white light, and combines with 4 measures of chlorine, producing hydrochloric acid and pentachloride of phosphorus.—$1\frac{1}{2}$ vol. hydrogen gas requires $1\frac{1}{2}$ vol. chlorine, and $\frac{1}{4}$ vol. vapour of phosphorus requires $2\frac{1}{2}$ vol. chlorine; and $1\frac{1}{2} + 2\frac{1}{2} = 4$. According to Thomson, one volume of the more inflammable gas consumes only 3 volumes of chlorine; but with the less inflammable, Davy found the ratio of 1 : 4.—5. Bromine precipitates phosphorus from the spontaneously inflammable gas, and forms hydrobromic acid, with evolution of heat. (Balard.)—6. Iodine introduced into the spontaneously inflammable gas produces iodide of phosphorus and hydriodic acid, together with free hydrogen. (Thomson.) The hydrogen was in all probability previously mixed with the gas.—7. Sulphur heated in the gas produces hydrosulphuric acid and sulphide of phosphorus. One volume of phosphuretted hydrogen gas should yield $1\frac{1}{2}$ vol. of hydrosulphuric acid gas; but as this gas is absorbed by sulphide of phosphorus, the quantity actually obtained is less. From one volume of the spontaneously inflammable gas, Thomson obtained one volume, and Vauquelin 1·1 volume of hydrosulphuric acid gas; while from one volume of the less inflammable gas, Dumas obtained 1·35, and Davy 2 volumes of hydrosulphuric acid gas.

8. Many metals, as potassium, zinc, iron, copper, and antimony, abstract phosphorus from the gas at high temperatures, forming metallic phosphides, and leaving $1\frac{1}{2}$ vol. of pure hydrogen gas. From one volume of the more inflammable gas, potassium separates 1·33 vol. of pure hydrogen, according to Sir H. Davy and Dalton, and 1·5 vol., according to Gay-Lussac & Thénard; with zinc or antimony, Buff likewise obtained 1·5 vol. One volume of the less inflammable gas yields with red-hot iron or copper, 1·49 and 1·52 vol. hydrogen gas (Dumas); with red-hot copper, 1·5 (Buff); with potassium [probably from the presence of moisture], 2 volumes. (H. Davy.)

9. Phosphoric oxide, sulphurous acid, sulphuric acid, chlorine water, hypochlorous acid, hypochlorite of lime, nitrous oxide, nitric oxide, nitric acid, arsenic acid, heavy metallic oxides, and their solutions in acids

decompose phosphuretted hydrogen gas. When this gas is passed through water in which phosphoric oxide is diffused, the latter becomes white, because, according to Mulder, a compound of phosphoric acid with phosphuretted hydrogen gas is produced,—more probably, however, because the two compounds are resolved into water and phosphorus. Sulphurous acid gas produces with the spontaneously inflammable gas, water and sulphide of phosphorus. Anhydrous sulphuric acid introduced into the more inflammable gas, produces sulphurous acid gas, with separation of phosphorus and sulphur; oil of vitriol with the same gas, forms sulphur, phosphorus, and hydrosulphuric acid. Hypochlorous acid gas detonates with spontaneously inflammable phosphuretted hydrogen, and aqueous hypochlorous acid yields phosphoric and hydrochloric acid. (Balard.) Solution of hypochlorite of lime (chloride of lime) acts in the same way. (Dalton.) Phosphuretted hydrogen gas detonates by the electric spark with nitrous oxide or nitric oxide gas; is slightly decomposed by hyponitric acid, but violently and with great evolution of heat by concentrated nitric acid. The spontaneously inflammable gas is decomposed by contact with arsenic acid (*Graham;* probably with formation of water and phosphide of arsenic); slowly by mercurous oxide, and not at all by mercuric oxide. (Graham.) By dinoxide or protoxide of copper slightly heated, it is easily resolved into water, phosphide of copper, and phosphoric acid. (H. Rose.) It precipitates lead-salts very slowly, copper-salts more quickly, and the salts of the noble metals most quickly of all. The precipitates are mostly black, and consist, sometimes of a metallic phosphide, as in the case of copper; sometimes of a combination of the metallic phosphide with the metallic salt, as with nitrate or sulphate of mercuric oxide, which give white precipitates; sometimes of reduced metal, the liquid retaining phosphoric acid, as in the case of silver and gold. (H. Rose.) The gas obtained from phosphorus and alcoholic solution of potassa does not precipitate the salts of antimony, bismuth, zinc, cadmium, tin, lead, iron, cobalt, nickel, copper (?), platinum, rhodium, or iridium from their aqueous solutions; but gives precipitates with solutions of tellurium, mercury, silver, gold, and palladium, the product in all cases being a metallic phosphide. It acts in a similar manner on dry nitrate of silver or protonitrate of palladium, whereas dry protonitrate of mercury or chloride of gold are not decomposed by it. (Böttger, *Beiträge*, 2, 116.)

10. Many metallic chlorides when gently heated in phosphuretted hydrogen gas, produce hydrochloric acid gas—the volume of which is three times as great as that of the phosphuretted hydrogen—and a metallic phosphide; or else hydrochloric acid, free phosphorus, and free metal. The spontaneously inflammable gas decomposes the chlorides of iron, cobalt, nickel, and copper, and likewise chloride of chromium, when a stronger heat is applied. (H. Rose.) Corrosive sublimate (HgCl) heated in either the more inflammable or the less inflammable gas till it sublimes, produces a violent action, and yields 3 measures of hydrochloric acid gas together with a yellowish-red powder; with the more inflammable gas, a slight action takes place even in the cold. (Dumas.) With solution of corrosive sublimate, both varieties of phosphuretted hydrogen give a yellow precipitate consisting of phosphide and chloride of mercury. (H. Rose.)

11. With chloride of phosphorus, phosphuretted hydrogen yields hydrochloric acid and phosphorus.

Combinations. *a.* With water.—Water freed from air by boiling absorbs, according to Gengembre, $\frac{1}{38}$ of its volume, according to W. Henry

$\frac{1}{47}$, according to Sir H. Davy, $\frac{1}{40}$, according to Dalton $\frac{1}{8}$, according to Raymond $\frac{1}{4}$ of its volume of the more inflammable,—and, according to Sir H. Davy $\frac{1}{8}$ of its volume of the less inflammable gas. Water thus charged smells like the gas: its taste is harsh, faint, and disagreeable, according to Raymond, and excessively bitter, according to Thomson. When boiled, it evolves the dissolved gas in its original state. It does not shine in the dark. When exposed to air (and perhaps also to light) it evolves hydrogen gas and deposits phosphoric oxide. It does not precipitate salts of manganese, zinc, or iron, but gives precipitates with salts of lead, copper, mercury, silver, and gold.

Other Compounds. *a.* With oil of vitriol.—*b.* With hydriodic acid.—*c.* With hydro-bromic acid.—*d.* With aqueous solution of ammonia?—*e.* With several metallic chlorides; *e. g.* Al^2Cl^3, $TiCl^2$, $SnCl^2$, $SbCl^3$. The compounds of phosphuretted hydrogen with hydriodic acid and metallic chlorides are analogous to those of ammonia: it is immaterial whether the more inflammable or the less inflammable gas is used in their preparation. (H. Rose.)—*f.* Phosphuretted hydrogen is absorbed by alcohol, ether, and volatile oils.

The difference of inflammability of the two varieties of phosphuretted hydrogen gas has been explained in three different ways.

1. The more inflammable gas contains—setting apart the free hydrogen, which is always mixed with it, and remains behind when the gas is agitated with solution of sulphate of copper—a larger quantity of phosphorus than the less inflammable. For this reason, the former has been called *Perphosphuretted Hydrogen gas* (*Phosphorwasserstoff-gas im Maximum*); the latter, *Protophosphuretted Hydrogen gas, Phosphorwasserstoff-gas im Minimum*). This view appeared to be confirmed by Dumas,—according to whose analyses, the former gas contains 2 atoms,—the latter, 3 atoms of hydrogen combined with one atom of phosphorus (see Dumas' analyses, p. 140). According to Dumas, the more inflammable gas, when kept for some weeks under water in a well-stopped bottle, is converted, with deposition of phosphorus, into an equal volume of the less inflammable; it likewise undergoes the same alteration when heated with alcohol. Leverrier's view is closely related to this. According to him, the more inflammable gas is a mixture of the less inflammable gas, PH^3, with more or less of the compound PH, or more probably PH^2. The latter, when submitted over water to the action of light, is resolved into PH, which is precipitated (p. 135), and PH^3, ($2PH^2 = PH + PH^3$); so that the less inflammable PH^3 is left in the pure state, and exposure to sunshine occasions no further deposit. These conclusions, Leverrier draws from the following experiments. The gas obtained by very gently heating a mixture of phosphorus and milk of lime, deposits nothing when kept in the dark in a vessel of thin glass over well-boiled water,—but retains its spontaneous inflammability. By exposure to daylight, however, the water in the course of two hours acquires a yellow colour, from decomposition of the absorbed gas and deposition of PH; upon this, the rest of the gas deposits PH—the more quickly in proportion to the strength of the light—and is thereby converted into the less inflammable gas. If the vessel is made of thick glass, the gas retains its spontaneous inflammability in weak daylight for three months in the winter; but in the brighter daylight of May, it is completely decomposed. When exposed to the sun's rays over water, the gas loses its spontaneous inflammability in two or three hours, and after six or eight hours, no longer

forms a cloud when it escapes into the air. The decomposition is accelerated by frequently washing off the yellow film with which the sides of the vessel become coated. The weight of the deposited PH amounts to about $\frac{1}{30}$ of the whole; consequently, that of the PH^2, from which it is probably formed, must be about $\frac{1}{15}$ of the gas employed. The spontaneously inflammable gas when perfectly dry remains quite unaltered in daylight; and even when it is exposed to full sunshine in the month of June, no alteration takes place for 60 hours; but by longer exposure, a partial decomposition is produced, by which the gas loses indeed its spontaneous inflammability, but produces white fumes when exposed to the air, and continues to deposit PH when exposed to light over water. It appears then that the resolution of PH^2 into PH and PH^3 is very much favoured by water. Water containing air slowly oxidizes, in the dark, a portion of the PH of the absorbed gas, and precipitates the rest; but its action is slower than that of light. (Leverrier.)

With these observations the following older experiments are in accordance. The spontaneously inflammable gas, when exposed to sunshine, deposits a red phosphoric substance. (A. Vogel.) It likewise deposits phosphorus when standing over water (containing air?) in the dark, especially on cooling, and subsequently does not take fire in the air at ordinary temperatures, excepting when brought in contact with the air in large quantity at once. (Vauquelin.)

2. According to H. Rose, both gases have the same composition, PH^3; so that their difference of inflammability must be attributed to isomeric conditions. It is true that the gas obtained by heating the aqueous solution of an alkali with phosphorus contains a larger quantity of phosphorus;—but that substance is present in the state of vapour only, perhaps existing as PH, and is deposited in the gas-delivery tube. If the gas, as it is evolved, is made to pass through a receiver and a long glass tube filled with chloride of calcium, care being taken to prevent explosion,—it deposits the excess of phosphorus (or perhaps PH); and if the gas thus obtained be collected in bottles which are filled either with mercury or with water deprived of air by boiling, then closely sealed, and exposed for two years even to the brightest sunshine, it deposits no more phosphorus, but retains its spontaneous inflammability. When phosphorus is heated in the less inflammable gas till it is converted into vapour, the gas shows no symptom of conversion into the spontaneously inflammable variety. But when kept for a long time over mercury at the ordinary atmospheric pressure, it sometimes acquires spontaneous inflammability. Moreover, according to H. Rose's analyses, the more inflammable gas, when freed from vapour of phosphorus, has the same specific gravity and the same composition, PH^3, as the less inflammable. The two gases likewise form with hydriodic acid and metallic chlorides, compounds having the same composition and the same properties; and these may be made to yield either the more or the less inflammable gas, according to the manner in which they are decomposed. Whether a metallic chloride be in combination with the more inflammable or the less inflammable gas, the former gas is always disengaged from the compound by the action of ammonia, and the latter by other liquids. (H. Rose.)

If this view is to be adopted, isomerism must not be understood in the narrow sense to which it is usually restricted (see I., 108); inasmuch as compounds which are isomeric in that sense exhibit differences in their combinations with other bodies, and in their other chemical relations—

which is not the case with the two forms of phosphuretted hydrogen. It is perhaps rather to be supposed that these gases exhibit *dimorphous* relations, and that if they could be reduced to the solid state, they would assume different crystalline forms. This hypothesis appears to receive some support from the analogous case observed by Frankenheim (I., 100), viz. that the vapour of red iodide of mercury appears to be different in its characters from that of the yellow iodide.

3. Graham founds his views on the fact demonstrated by Rose—that the two gases have the same composition, PH^3; but he explains their difference of inflammability, not by the existence of two isomeric states, but by the admixture of foreign substances. He finds that perfectly pure phosphuretted hydrogen gas is not spontaneously inflammable; but that traces of foreign bodies may give it spontaneous inflammability, and others again may deprive it of this property. Graham's experiments were made with spontaneously inflammable gas prepared by heating milk of lime with phosphorus, and with the less inflammable gas obtained by heating hydrated phosphorous acid.

a. The less inflammable may be converted into the more inflammable gas by admixture of a trace of nitrous acid vapour, in the following ways. 1. A small glass bulb filled with nitrous acid is introduced into the less inflammable gas over mercury: the acid evaporates, forming a small white cloud. The mixture thus obtained is not itself spontaneously inflammable, because it contains too large a quantity of nitrous acid; but it will impart spontaneous inflammability to large quantities of the less inflammable gas. One volume of nitrous acid vapour is sufficient to convert from 1000 to 10,000 volumes of the less inflammable gas into the more inflammable.—2. A drop of concentrated nitric acid is introduced into the gas as it stands over mercury; the acid by its action on the mercury produces nitrous acid.—3. The less inflammable gas is passed through a mixture of one measure of English oil of vitriol (which generally contains a little nitrous acid) and 3 measures of water immediately after cooling, and before the nitrous acid contained in it has had time to escape into the air.—4. Pure hydrogen gas mixed with the less inflammable phosphuretted hydrogen does not, as already shown by Rose, make it spontaneously inflammable. But if the hydrogen gas contains a trace of nitrous acid, it possesses this property. Such hydrogen gas is obtained by dissolving zinc or iron in a mixture of water and common oil of vitriol containing nitrous acid;—it is only the first portions of gas evolved that contain nitrous acid, and are consequently efficacious in this respect. One measure of hydrogen thus charged with nitrous acid imparts spontaneous inflammability to between $\frac{1}{3}$ vol. and 1 vol. of the less inflammable gas. The same result is obtained by passing pure hydrogen gas through a mixture of one measure of common oil of vitriol and 3 measures of water, immediately after cooling,—or by placing hydrogen gas in contact with a freshly prepared mixture of fuming nitric acid and water. Pure nitric oxide gas freed by washing with caustic potash from vapours of nitrous acid does not, in any proportion, communicate spontaneous inflammability to the less inflammable gas; but one volume of unwashed nitric oxide gas forms—in consequence of the nitrous acid which is mixed with it—a spontaneously inflammable mixture with 1000 to 2000 volumes of the less inflammable gas; but when the proportion of nitric oxide is greater than $\frac{1}{1000}$ or less than $\frac{1}{2000}$, this effect is not produced.

The gas which has acquired spontaneous inflammability by mixture with nitrous acid loses this property in a week when left standing over

mercury (which decomposes the nitrous acid); over water, a longer time is required. The power of taking fire spontaneously is quickly lost by contact with potassium-amalgam, phosphorous acid, oil of vitriol (which probably absorbs the nitrous acid), charcoal, and volatile oils, slowly in contact with solution of potassa, not at all by contact with phosphoric acid.

b. The more inflammable gas loses its spontaneous inflammability under the following circumstances: 1. When kept over water containing air, the change not being attended with deposition of phosphorus; or, when mixed with a very small quantity of air,—the presence of cork or gypsum, which contain air in their pores, being sufficient to effect the change.—2. The admixture of about 5 volumes of hydrogen, 2 of carbonic acid, 1 of olefiant gas, $\frac{1}{2}$ a volume of hydrosulphuric acid, $\frac{1}{8}$ of ammoniacal gas, $\frac{1}{10}$ of nitric oxide, or $\frac{1}{20}$ of hydrochloric acid gas, with one volume of the more inflammable gas, destroys its spontaneous inflammability. The gas mixed with $\frac{1}{10}$ of nitric oxide gives red vapours in the air; that mixed with $\frac{1}{20}$ of its volume of the same gas takes fire with a kind of detonation, while the bubble is rising in the air.—3. Concentrated phosphoric, sulphuric, or arsenic acid, when the sides of the containing vessel are moistened with them, destroy the spontaneous inflammability of the gas in two or three minutes, the change being attended with partial mutual decomposition; arsenious acid and mercurous oxide act quickly; solution of potash not till after some hours.—4. Potassium, by itself, or even a solution of 1 grain of it in 50 lbs. of mercury (the gas standing over it), destroys the spontaneous inflammability in a few minutes.—5. One volume of charcoal cooled by plunging it when red-hot into mercury, and then introduced into 500 measures of the more inflammable gas, absorbs 10 volumes of it in five minutes, and brings the rest to the less inflammable state in half an hour, probably by absorbing the peculiar principle which causes the spontaneous inflammability. The charcoal when heated, evolves the less inflammable gas. In 50 volumes of gas the action of 1 volume of charcoal is complete in five minutes. Burnt clay exerts a similar action. On the contrary, charcoal quenched in water, as also spongy platinum, red oxide of mercury, and solution of proto-sulphate of iron, do not remove the spontaneous inflammability.

After all, the spontaneously inflammable gas must contain a peculiar substance which gives it this character: this substance cannot be nitrous acid; it is probably a lower degree of oxidation of phosphorus. (So far Graham.)

When the spontaneously inflammable gas contained in a glass tube over mercury is strongly heated by means of charcoal, it does not deposit phosphorus, but loses its spontaneous inflammability. (A. Vogel, *J. pr. Chem.* 6, 348.)

¶ Paul Thénard has shown that the more inflammable phosphuretted hydrogen owes its spontaneous inflammability to the presence of a small quantity of a liquid phosphide of hydrogen, PH^2, to be described immediately. By exposure to light, or by the presence of hydrochloric acid and certain volatile chlorides, this liquid phosphide is resolved into the solid phosphide, which is deposited as a yellow powder, and gaseous phosphuretted hydrogen. The gas then loses its spontaneous inflammability. Phosphuretted hydrogen gas PH^3, when perfectly pure, is not spontaneously inflammable at ordinary temperatures: it may be obtained in a state of purity by the action of strong fuming hydrochloric acid on

phosphide of calcium, a considerable quantity of the solid phosphide being formed at the same time.

Rose observes—in confirmation of his idea, that the two varieties of phosphuretted hydrogen are isomeric—that they form identical compounds with certain metallic chlorides, and that, accordingly as these compounds are decomposed by water or by an ammoniacal liquid, the gas evolved belongs to the less inflammable or the more inflammable variety. Thénard, however, has shown that when the compound of phosphuretted hydrogen with bichloride of tin or of titanium is decomposed by an ammoniacal liquid, a rise of temperature is produced, whereby the gas is heated above 100°, and consequently takes fire as it escapes into the air. If the tube containing the gas be artificially cooled, this effect does not take place. (Paul Thénard, *N. Ann. Chim. Phys.* 14, 5.)

C. Liquid Phosphide of Hydrogen. PH^2.

Formation. (1.) By the mutual action of water and the so-called *Phosphide of Calcium.* This latter substance, which is obtained by the action of vapour of phosphorus upon lime at a red-heat, has been shown by Paul Thénard to be a mixture of phosphide of calcium and phosphate of lime: $2\,(PO^5, 2CaO) + 5PCa^2$. When it is put into water, the 5 atoms of phosphide of calcium, PCa^2, and 10 atoms of water, produce 10 atoms of lime and 5 atoms of liquid phosphide of hydrogen:

$$5PCa^2 + 10HO = 10CaO + 5PH^2.$$

(2.) By deposition from spontaneously inflammable phosphuretted hydrogen gas.

Preparation. Into the middle tubulure of a three-necked Woulfe's bottle, holding about a pint, is inserted a glass tube 12 inches long and half an inch wide, so as to reach nearly to the bottom. To the second tubulure is adapted a tube twice bent at right angles; this tube dips into water and serves for a safety-tube. Into the third is fitted a tube of $\frac{1}{4}$ inch diameter, which serves first for a condenser and then for a receiver; it is bent *U*-shape, so that it may be immersed to the depth of 5 or 6 inches in a freezing mixture. The part which projects above the freezing mixture is bent at a not very acute angle, and drawn out at two points not far from each other and near the end, so that, at the conclusion of the operation, the liquid may be introduced into the intermediate part of the tube, and the parts which have been drawn out closed by the blowpipe. The apparatus being thus arranged, the bottle is three parts filled with water and placed in a water-bath heated to between 140° and 160° F. The last-mentioned tube is closed, and a few drops of phosphide of calcium thrown through the middle one into the bottle. The gas evolved takes fire, and drives out the air through the safety-tube. The *U*-shaped tube is now to be opened, and from 400 to 600 grains of phosphide of calcium gradually introduced into the bottle: in a few minutes, oily drops of liquid are seen to collect in the part of the tube nearest to the bottle. The process must be stopped after 15 or 20 minutes, because water condenses in the tube together with the phosphide of hydrogen, and often stops it up. The tube is now to be sealed at the narrowed neck nearest to its extremity, then removed from the bottle, and held by the finger (covered with caoutchouc to save the operator from being burnt) in such a position that any remaining gas may escape; it is then warmed by the

hand to cause the portions of liquid which have been separated by particles of ice to run together, and again placed in the freezing mixture to solidify the water, and prevent it running back. This being effected, the liquid is made to flow towards the sealed end of the tube, and the other neck of the tube closed by the blowpipe. A well-conducted operation yields about 30 grains of liquid.

Properties. Colourless liquid, not solidifying at $-20°$ C.; at 30° or 40°, it appears to volatilize and to be decomposed at the same time. Refracts light strongly. Insoluble in water. Alcohol and oil of turpentine appear to dissolve it, but it quickly decomposes in the solution. Burns in the air with an intensely bright white flame, and produces dense white fumes. Communicates spontaneous inflammability to 500 times its weight of the less inflammable phosphuretted hydrogen gas, the latter thereby acquiring all the properties of the more inflammable gas. All combustible gases are rendered spontaneously inflammable by admixture with liquid phosphide of hydrogen.

The composition of this substance is

	By Calculation.	
P	31·7	94·07
2H	2·0	5·93
PH^2	33·7	100·00

Decompositions. By the action of light it is resolved into solid (P^2H) and gaseous phosphide of hydrogen (PH^3):

$$5PH^2 = P^2H + 3PH^3.$$

It is also decomposed, like peroxide of hydrogen, by contact with various substances. An indefinite quantity of liquid phosphide of hydrogen may be decomposed by a cubic centimetre of hydrochloric acid gas.¶

Phosphorus and Carbon.

Phosphide of Carbon? This compound is obtained, according to Thomson (*Ann. Phil.* 8, 157), when phosphide of calcium is decomposed by water, and the lime dissolved out by excess of hydrochloric acid; phosphide of carbon then remains behind, and must be collected on a filter and quickly washed. It is a brownish-yellow, soft, tasteless, inodorous, and infusible powder. According to Thomson, it contains 38 carbon + 62 phosphorus. It suffers no alteration in dry air below 100°, but takes fire at a red heat, the phosphorus burning to phosphoric acid, while the carbon remains unburnt. It attracts water from the air, forming carburetted hydrogen gas and carbonic acid. (Thomson.) It is probably a mixture of phosphoric oxide and charcoal, which latter substance is perhaps separated from carbonic acid remaining in the lime.

A similar substance remains behind when the crude phosphorus obtained by the distillation of calcareous phosphoric acid is pressed through chamois leather (p. 104). When the free phosphorus is separated from this substance by distillation, and the orange-yellow residue is heated to redness (at which temperature the phosphoric oxide is decomposed), it evolves phosphorus and leaves charcoal behind. (Berzelius, *Lehrb.* 1, 312.)

Phosphuretted Carbonic oxide gas? When phosphorus is prepared by distilling phosphoric acid with charcoal (p. 104), the whole of the phos-

phorus does not condense in the receiver, but a portion remains dissolved in the gas which is evolved. This, when freed from carbonic acid by agitation with milk of lime, is of about the same specific gravity as common air—has a disagreeable odour—does not redden litmus—does not deposit phosphorus, even after long standing—exhibits no luminosity when brought in contact with oxygen gas—burns with that gas at an elevated temperature with less forcible explosion than hydrogen, and with a white flame, producing phosphoric acid, carbonic acid, and water. It reduces gold and silver from their solutions in acids. Trommsdorff (*A. Tr.* 10, 1, 30), who first distinguished this gas, regards it as a compound of phosphorus, carbon, and hydrogen, and calls it *Phosphuretted Carburetted Hydrogen gas.* It is probably a mixture of carbonic oxide, hydrogen, and phosphuretted hydrogen.

Phosphorus with Phosphorus.

Phosphate of Phosphoric Oxide, or Phosphoric Phosphate.

The yellow film of phosphoric phosphate, which is produced in the preparation of phosphoric oxide by the fifth method (p. 111), is freed from adhering phosphorous acid and hydrochloric acid, by washing it in the flask in which it has been deposited—first, with ether, which removes the greater portion of the free acids, and then with absolute alcohol, which dissolves the rest of the free acids, together with the phosphoric phosphate and a small quantity of phosphorus. The liquid filtered from the undissolved phosphorus is mixed with absolute ether, which retains in solution the phosphorus and the free phosphoric, phosphorous, and hydrochloric, acids, but precipitates the phosphoric phosphate. This precipitate is washed with ether, and—in order to purify it completely—again dissolved in alcohol and precipitated by ether. It is then put into a dish—the greater part of the ether removed by means of a pipette—and the rest left to evaporate in vacuo over oil of vitriol. The phosphoric phosphate remains behind, mixed with a small quantity of organic matter from the ether, which cannot be removed.

This substance is of an orange-yellow colour, easily pulverized, inodorous, and has a very faint taste.

Its composition is about $4P^2O, 3PO^5$

It resolves itself spontaneously, after a time, into phosphoric acid and phosphoric oxide. When newly prepared, it is completely soluble in water; but the yellow solution deposits hydrated phosphoric oxide, after a few hours at ordinary temperatures, and immediately at 80°. The still undecomposed aqueous solution is coloured deep brown, without precipitation, by caustic potassa, possibly from formation of a double phosphate of potassa and phosphoric oxide; but on the application of heat, phosphoric acid is precipitated in combination with a certain portion of potassa. Alcohol completely dissolves freshly prepared phosphoric phosphate, forming a yellow solution. (Leverrier, *Ann. Chim. Phys.* 65, 257.)

Other Compounds of Phosphorus.

A. With sulphur.—B. With selenium.—C. With iodine.—D. With bromine.—E. With chlorine.—G. With nitrogen.

H. With most metals, forming compounds called *Phosphides* or

Phosphurets. The affinity of phosphorus for metals is not so strong as that of sulphur. Metallic phosphides are formed: 1. By bringing the phosphorus and the metal together at elevated temperatures, the combination being often attended with development of light and heat.—2. By igniting the metal in contact with phosphoric acid, either pure or containing lime, and either with or without charcoal, the charcoal or a portion of the metal taking up the oxygen of the phosphoric acid. 3. By heating certain metallic oxides in contact with phosphorus; part of the phosphorus then combines with the oxygen to form phosphoric acid,—the rest with the metal, to form a metallic phosphide.—4. By igniting a metallic phosphate with charcoal.—5. By bringing phosphuretted hydrogen in contact with metallic chlorides, oxides, and their salts.

The metallic phosphides are solid and almost all brittle; they generally exhibit the metallic lustre, and are opaque. At very high temperatures, many metals give up their phosphorus. In some phosphides, the phosphorus alone oxidates in the air at ordinary temperatures—in others, the metal likewise oxidates. At high temperatures, combustion of the phosphorus always takes place, sometimes attended with the formation of the corresponding phosphate. Nitric or hypochlorous acid converts the phosphides into phosphates. The compounds of phosphorus with the alkali-metals decompose water, producing phosphuretted hydrogen gas, hypophosphorous acid, and a metallic oxide.

I. With alcohol, ether, volatile, and fixed oils, wax, and resins.

Chapter VI.

SULPHUR.

Sulphur in general:

H. Davy. *Phil. Trans.* 1809, I., 59; *Schw.* 1, 473, 484, also *Gilb.* 35, 278; 36, 184. Further, *Schw.* 7, 508; also *Gilb.* 36, 184.

Gay-Lussac & Thénard. *Recherches*, 1, 187; also *Ann. Chim. Phys.* 73, 229; also *Schw.* 1, 488; also *Gilb.* 35, 292.

Dumas. *Ann. Chim. Phys.* 36, 83; also *N. Tr.* 17, 1, 197.

Marchand & T. Scheerer. *J. pr. Chem.* 24, 129.

Hyposulphurous acid:

Gay-Lussac. *Ann. Chim.* 85, 199.

Herschel. *Ed. Phil. J.* 1, 8 and 396; 2, 154; also *N. Tr.* 5, 2, 308.

Kessler. *Pogg.* 74, 274; abstr. *Ann. Pharm.* 68, 231.

Pentathionic acid:

Wackenroder. *Archiv. der Pharm.* 47, 272; 48, 140; abstr. *Ann. Pharm.* 60, 189.

Lenoir. *Ann. Pharm.* 62, 253.

Fordos & Gélis. *N. Ann. Chim. Phys.* 22, 66; abstr. *Ann. Pharm.* 64, 249.

Kessler. *Pogg.* 74, 249; abstr. *Ann. Pharm.* 68, 231.

Tetrathionic acid:

Fordos & Gélis. *Compt. Rend.* 15, 920; *Ann. Pharm.* 44, 217.
Kessler. *Pogg.* 74, 249.

Trithionic acid:

Langlois. *Compt. Rend.* 10, 461; also *J. pr. Chem.* 20, 61.—Further: *Ann. Chim. Phys.* 79, 77; also *Ann. Pharm.* 40, 102.
Pelouze. *Ann. Chim. Phys.* 79, 85.
Kessler. *Pogg.* 74, 249.

Sulphurous acid:

Fourcroy & Vauquelin. *Ann. Chim.* 24, 229; also *Crell. Ann.* 1800, 2, 299 and 388 (the end of this memoir is wanting).
Bussy. *J. Pharm.* 10, 202; also *Ann. Chim. Phys.* 26, 63; also *Schw.* 41, 451; *Pogg.* 1, 237; *Kastn. Arch.* 2, 127 and 241; *Mag. Pharm.* 7, 160; *Berl. Jahrb.* 26, 2, 45.
Delarive. *Bibl. Univ.* 40, 196; also *N. Tr.* 20, 1, 197; abstr. *Pogg.* 15, 523; abstr. *Schw.* 55, 232.
Sulphites. Muspratt. *Ann. Pharm.* 49, 259. Further: *Phil. Mag. J.* 30, 414. Rammelsberg. *Pogg.* 67, 245.

Hyposulphuric acid:

Welter & Gay-Lussac. *Ann. Chim. Phys.* 10, 312; also *Schw.* 29, 182; also *Gilb.* 65, 252. Heeren, *Pogg.* 7, 55.
Rammelsberg. *Pogg.* 58, 295; abstr. *Ann. Pharm.* 48, 207.

Sulphuric acid:

Formation. Clement & Desormes. *Ann. Chim.* 59, 329; also *N. Gehl.* 4, 456. Peligot. *N. Ann. Chim. Phys.* 12, 263.
Anhydrous. F. C. Vogel. *Schw.* 4, 121.—Bussy, *Ann. Chim. Phys.* 26, 411; also *J. Pharm.* 10, 368; also *Mag. Pharm.* 8, 69; also *N. Tr.* 9, 2, 65.—Wach. *Schw.* 50, 1.—H. Rose. *Pogg.* 39, 173.—Barreswil. *Compt. Rend.* 25, 30.
Sulphates. Gay-Lussac. *Mém. d'Arcueil,* 1, 215; also *N. Gehl.* 4, 465; also *Gilb.* 27, 86. Further: *Ann. Chim. Phys.* 63, 431; also *Ann. Pharm.* 22, 305; also *J. pr. Chem.* 11, 65.—Graham. *Phil. Mag. J.* 6, 329. *Ann. Pharm.* 29, 27.

Persulphide of Hydrogen:

Scheele. *Von der Luft und von dem Feuer,* 153.—Berzelius. *Lehrb.* 2, 218.—Thénard. *Ann. Chim. Phys.* 48, 79; also *Schw.* 64, 231; also *Ann. Pharm.* 2, 11; also *N. Tr.* 25, 2, 198.—Liebig. *Ann. Pharm.* 2, 27; 18, 170.

Hydrosulphuric acid:

Scheele. *Opuscula,* 1, 132.—Berthollet. *Scher. J.* 1, 367.—Fourcroy. *Crell. Ann.* 1793, 2, 64.—A. Vogel. *J. Phys.* 82, 329.—Bischof. *Schw.* 39, 38.—H. Rose. *Pogg.* 47, 161.—Action of Hydrosulphuric acid on Fish. Blanchet. *Ann. Pharm.* 53, 109.

Bisulphide of Carbon:

Lampadius. *A. Gehl.* 2, 192.—Clement & Desormes. *Ann. Chim.* 42, 121; also *Scher. J.* 7, 10, 512; also *Gilb.* 13, 73.—Trommsdorff. *A. Tr.* 17, 1, 29.—Am. Berthollet. *Gilb.* 28, 427.—Vauquelin & Robiquet. *Ann. Chim.* 61, 145; also *N. Gehl.* 4, 12; also *Gilb.* 28, 453.—Cluzel. *Ann. Chim.* 84, 72.—Berthollet, Thénard & Vauquelin. *Ann. Chim.* 83, 252; also *Schw.* 9, 301.—Berzelius & Marcet. *Schw.* 9, 284; also *Gilb.* 48, 135; Kolbe. *Ann. Pharm* 45, 41.—Berzelius. *Gilb.* 48, 177; also *Schw.* 34, 75.—Zeise. *Schw.* 36, 1; 41, 98 and 170; 43, 160.—Berzelius. *Pogg.* 6, 444.—Couerbe. *Ann. Chim. Phys.* 61, 225; abstr. *J. pr. Chem.* 23, 83.

Sulphide of Boron. Berzelius. *Pogg.* 2, 125.

Sulphides of Phosphorus. Marggraf. *Chym. Schrift,* 1, 47.—Pelletier. *Ann. Chim.* 4, 1.—Faraday. *Ann. Chim. Phys.* 7, 71.—R. Böttger. *Schw.* 67, 141; 68, 136.—*J. pr. Chem.* 12, 357.—Levol. *Ann. Chim. Phys.* 67, 332; also *J. pr. Chem.* 15, 119.—A. Dupré. *Ann. Chim. Phys.* 73. 435; abstr. *J. pr. Chem.* 21, 253.—Berzelius. *Ann. Pharm.* 46, 129, 255; also *Traité de Chimie,* Par. 1845, I., 815.

Metallic Sulphides:

Alkaline Sulphides. Vauquelin. *Ann. Chim. Phys.* 6, 5; also *N. Tr.* 2, 2, 270.—Thénard. *Ann. Chim.* 83, 132; also *Gilb.* 44, 94. Gay-Lussac. *Ann. Chim.* 78, 86; also *Gilb.* 41, 328; also *Schw.* 24, 234.—*Ann. Chim. Phys.* 6, 321; also *N. Tr.* 3, 1, 195.—*Ann. Chim. Phys.* 30, 24; also *N. Tr.* 12. 2, 195.—Berzelius. *Schw.* 34, 1.—Berthier. *Ann. Chim. Phys.* 22, 225; also *N. Tr.* 9, 1, 66.—*Ann. Chim. Phys.* 24, 273; also *Mag. Pharm.* 5, 284.—H. Rose. *Pogg.* 55, 415.

Heavy Metallic Sulphides and Sulphur-salts. Deiman, Troostwyk, Nieuwland, Bondt, & Lauwerenburgh. *Crell. Ann.* 1793, 2, 383.—Arfvedson. *Pogg.* 1, 49; also *N. Tr.* 10, 2, 144.—Berzelius. *Pogg.* 6, 425.

Soufre, Schwefel.

History. Sulphur has been known from the earliest times. The Arabians were perhaps acquainted with sulphuric acid; but Basil Valentine is the first who mentions its preparation from green vitriol: the formation of this acid by the burning of sulphur was first brought into use in England in the year 1720. The white substance obtained by distilling fuming oil of vitriol, and long known by the name of *Ice-oil* (*Eis-öl*), or *Oleum glaciale Vitrioli,* was regarded by Dollfuss (*Crell. Ann.* 1785, 1, 438) and Fourcroy (*Crell. Ann.* 1791, 1, 363), as concentrated sulphuric acid combined with sulphurous acid; by Winterl, as sulphuric acid combined with excess of oxygen; by F. C. Vogel, as sulphuric acid deprived of the greater part of its water, and combined with an imponderable ethereal principle; but the experiments of Vogel, as well as those of Döbereiner (*Schw.* 13, 476), C. G. Gmelin (*Schw.* 27, 439), Ure (*Quart. J. of Sc.* 19, 62), and Bussy (*J. Pharm.* 10, 368), established the view already put forth by Scheele (*Opusc.* 2, 284), and Guyton-Morveau (in his *Grundsätzen über die sauren Salze,* I., 179), and now universally admitted, viz., that this substance must be regarded as anhydrous sulphuric acid.—The proportional composition of sulphuric acid was examined principally by Richter, Klaproth, Bucholz, and Berzelius.—Sulphurous acid, the compound

long known to be formed in the combustion of sulphur, was first examined minutely by Stahl; in 1771 by Scheele; in 1774 by Priestley, who first collected it as a gas over mercury; in 1782 and 1789 by Berthollet; and in 1797 by Fourcroy & Vauquelin, who made known the properties of many of its salts. Monge & Clouet first obtained sulphurous acid in the liquid state, in which form it was examined chiefly by Faraday, Bussy, Wach, and Delarive.—The hyposulphites were first examined by Vauquelin (*Crell. Ann.* 1800, 2, 286), afterwards by Gay-Lussac and Herschel.—Welter and Gay-Lussac discovered hyposulphuric acid; Langlois discovered sulphuretted hyposulphuric acid, otherwise called trithionic acid; tetrathionic acid was discovered by Fordos & Gélis; pentathionic acid by Wackenroder.

Persulphide of hydrogen, discovered by Scheele, has been more particularly examined by Berzelius, Thénard, and Liebig.—Hydrosulphuric acid was first discovered by Rouelle, but more minutely examined as to its composition by Scheele: subsequently, its chemical relations were further investigated, principally by Bergmann, Kirwan, Berthollet, Proust, Thénard, Gay-Lussac, Berzelius, and Sir Humphry Davy.

Bisulphide of carbon, discovered by Lampadius in 1796, was by him and by Am. Berthollet pronounced to be a compound of sulphur and hydrogen, and by Cluzel, a compound of sulphur with carbon, hydrogen, and nitrogen; but the experiments of C. L. Berthollet, of Thénard & Vauquelin, and of Berzelius & Marcet, have shown that it is really composed of sulphur and carbon, as first announced by Clement & Desormes.—Zeise discovered the acids produced by treating bisulphide of carbon with alkalis and alcohol, viz., the hydrosulphocarbonic, hydrosulphocyanic, and xanthonic acids.

Berzelius discovered sulphide of boron. Sulphide of phosphorus, first prepared by Marggraf, was further examined by Pelletier, Faraday, Mitscherlich, Böttger, Levol, and Dupré. The sulphides of phosphorus have subsequently been subjected to complete examination by Berzelius.

The development of light and heat, which frequently accompanies the combination of sulphur with metals, was long ago observed by Scheele; but Deiman, Troostwyk, Nieuwland, Bondt & Lauwerenburgh first showed that this combustion takes place equally well when air is excluded. The nature of *livers of sulphur* was principally investigated by Vauquelin, Gay-Lussac, and Berzelius. The latter, moreover, examined the other metallic sulphides with the greatest accuracy, and laid the foundation of the theory of the Sulphur-salts.

Occurrence in nature. 1. Native. 2. As sulphurous acid. 3. As sulphuric acid. 4. As hydrosulphuric acid. 5. In the metallic sulphides. 6. In certain organic compounds.

Preparation. 1. Native sulphur is separated by distillation from the earthy matters with which it is mixed. In Sicily, the volcanic sulphur is distilled in large earthen pots provided with a beak on the side.—2. From iron-pyrites or copper-pyrites, a portion of the sulphur is expelled by heating, the process being conducted—*a. By roasting the ore in heaps* (*Röst-haufen*). A square surface is covered with a few layers of billet-wood, and upon this the copper-pyrites, coarsely pounded, is heaped in the form of a truncated pyramid. The sides of this pyramid are covered with a layer of earthy matter to render them impervious to draught. Fire is applied to the wood by a channel which passes downwards through the

middle of the pyramid; thence it is communicated to the ore, and gradually extends to the whole mass. The sulphur contained in the ore is partly burnt and converted into sulphurous acid, partly rises in vapour to the upper truncated surface of the pyramid, and there condenses in hollows formed for the purpose and covered at the bottom with smooth earth. From these it is from time to time removed. (Schlüter, *Unterricht von Hüttenwerken*, 154.)—*b. In the roasting furnace* (*Röstöfen*). The ore is piled up upon wood between four walls perforated with holes at the bottom; it is then covered with earth. When the wood is set on fire, the draught of air produced by side-tubes opening into the furnace at its upper part carries the sulphur vapour into a condensing chamber. (Ferber, *Beiträge, zur Mineral-geschichte*, I., 220.) If the furnace is high and narrow, fresh ore may be introduced at the top as fast as that which is burnt is taken away at the bottom. In that case, the covering is formed, not of earth, but of solid plates, and the roasting is carried on without interruption. When once the ore has been set on fire by means of wood or coal, the combustion extends itself through the entire mass. (*Bergmännisches J.* 3, 1.)—*c.* A number of tubes of earthenware or cast-iron, called *Sulphur-tubes*, are laid very slightly inclined to one another in a common furnace. (*Schwefel-treiböfen oder Schwefel-brennöfen.*) They are filled with iron-pyrites through the upper and wider opening, which is closed while the combustion is going on. From the lower and narrower opening the sulphur flows into a cast-iron receiver (*Vorsetz-Kästchen*). The protosulphide of iron (*die Schwefel-brände*), which, after the combustion, is to be taken out by the upper opening, serves for the fabrication of green vitriol. (Schlüter, *Unterricht von Hüttenwerken*, 37.)

Purification. The *Crude-Sulphur* (*Roh-schwefel* or *Treib-schwefel*) obtained in this manner may be mixed with earthy matters and particles of the ore, and may also contain sulphide of arsenic, selenide of sulphur, and asphalt. It may be purified as follows:—(1.) *By fusion and decantation.* The sulphur is melted in a cast-iron vessel, the coarser particles removed by means of a perforated ladle, and the sulphur after standing for some time, poured off from the finer particles which have fallen to the bottom. This mode of purification is the least effective. (2.) By distillation in the *Sulphur-purifying furnace* (*Schwefelläuter-öfen*). This, according to the old arrangement, is a reverberatory furnace, on the two sides of which a number of cast-iron vessels, called *Purifying vessels* (*Läuter-krüge*), are placed on benches. They are filled with crude sulphur, and provided with an iron or earthenware head (*Sturz*), the beak of which passes into a receiver placed outside the furnace. (Schlüter, *Unterr. von Hüttenwerken*, 39.) In the new arrangement invented by Michel, the sulphur is heated to the boiling point in a large cast-iron boiler over which an arch of brickwork is raised. The vapour passes sideways through a wide brick channel into a chamber likewise formed of brick-work, where it condenses, first in the form of flowers of sulphur; but afterwards, if the process be continued uninterruptedly night and day, and the temperature of the chamber thereby raised to the melting point of sulphur, it collects at the bottom in the fused state, and may be drawn off by an opening in the side. (*Dictionn. Technolog.* Paris, 1831, 19, 491.) (3.) *By Sublimation.*—This process may likewise be conducted in Michel's apparatus; only it must be more frequently interrupted, so that the chamber may not get too hot; the sulphur collects on the walls in the state of fine powder.

The sulphur, after being purified by fusion or distillation, is cast in damp wooden moulds, sometimes in cheese-shaped masses, called *Loaves of Sulphur* (*Schwefel-brode*); sometimes in sticks, in which state it is called *Rolled Sulphur* (*Stangen-schwefel, Sulphur citrinum*). The sublimed sulphur is called *Flowers of Sulphur* (*Schwefel-blumen, Flores Sulphuris*); it requires to be washed with water to free it from adhering sulphurous and sulphuric acids.

Sulphur purified by method 1. may still contain portions of earth and ore; and that which is purified by either of the methods 1, 2, or 3, may retain arsenic, sulphur, and bituminous matters. (Vauquelin. *Ann. Chim. Phys.* 25, 50.) By repeated fractional distillation, whereby these substances, being less volatile, are partially left behind, the sulphur becomes continually purer. According to Osann (*Kastn. Arch.* 4, 344), it requires five or six distillations to render it sufficiently pure to sublime without leaving a carbonaceous residue.

Rolled sulphur, when heated by itself, and flowers of sulphur heated in contact with water, evolve hydrosulphuric acid gas. (Payen, *J. Pharm.* 8, 371.) Moist sulphur evolves hydrosulphuric acid when heated. (Pleischl. *Kastn. Arch.* 4, 340.) Sulphur, when it enters into combination with metals (copper, for example) evolves 0·1 per cent., or a smaller quantity, of hydrogen gas: but if it has previously been fused by itself, it evolves no more than a mere trace of that substance. (Dumas, *Ann. Chim. Phys.* 50, 176.) It appears from this that sulphur contains either hydrosulphuric acid in a state of condensation, or else persulphide of hydrogen; or again, the hydrogen may proceed from asphaltum or water contained in the sulphur.

The presence of arsenic in sulphur is detected, according to Berzelius, by digesting the sulphur in the state of fine powder with hydrochloric acid, evaporating to dryness, exhausting the residue with alcohol, and precipitating the arsenic from the filtrate by means of zinc. A similar process is adopted by Westrumb, who however uses a mixture of hydrochloric and nitric acid. Geiger & Reimann (*Mag. Pharm.* 19, 139) digest the finely divided sulphur, with agitation, in ammonia, and filter. If the filtrate contains much sulphide of arsenic, that substance is immediately precipitated from the filtrate on the addition of hydrochloric acid; but if the quantity of sulphide of arsenic is small, precipitation does not take place unless the liquid be previously mixed with a small quantity of potassa and evaporated to a few drops. From pure sulphur ammonia extracts nothing.

Selenium is detected in sulphur by dissolving the whole in boiling caustic potassa, or by fusing it with carbonate of potassa and dissolving the fused mass in water. The filtrate, after several days' exposure to the air, deposits selenium.

Properties. Solid sulphur is dimorphous (I., 98), and amorphous (I., 104).

a. Native sulphur and that which crystallizes from solution in bisulphide of carbon* takes the form of acute rhombic octohedrons. (*Fig.* 41—44, and others.) $a : a' = 84° 58'$; $a' : a^3 = 143° 17'$; $u : u' = 78° 1'$;

* Sulphur crystallized from bisulphide of carbon sometimes, though rarely, exhibits the oblique prismatic as well as the octohedral form of crystallization. The prismatic crystals take the primary form without any modification. They are at first transparent, and of the same yellow colour as the octohedral crystals, but soon become opaque, crumbly, and nearly white. (Pasteur, *Compt. Rend.* 26, 48.) [W.]

$a': p = 108° 21\frac{1}{2}'$. Cleavage parallel to the *a*-faces. (Mitscherlich, *Ann. Chim. Phys.* 24, 265.) Specific gravity, 2·0454 : of native sulphur, 2·033, *Brisson;* 2·050, *Karsten;* 2.062—2·070, *Marchand & Scheerer;* 2·072, *Mohs;* of sulphur crystallized from solution in bisulphide of carbon, 1·9727, *Bischof;* 2·050, *Marchand & Scheerer;* of rolled sulphur, 1·868, *Böckmann;* 1·990, *Brisson;* 1·977—2·000, *Thomson;* of flowers of sulphur, at 4° in vacuo, 2·086, *Le Royer & Dumas.* Very brittle and friable; decrepitates from formation of cracks when warmed in the hand. Colour, pale greenish-yellow, becoming orange-yellow when heated. Transparent or translucent. Its refracting power is to that of water as 0·204 : 0·1336. (Wollaston.) Does not conduct electricity; becomes electrical when rubbed with other bodies. Exhales a faint odour when rubbed, and has a scarcely perceptible taste.

b. When melted sulphur is allowed to cool slowly till it is half solidified, a hole then made in the crust, and the yet liquid portion poured out, the sulphur is obtained in very long and thin oblique rhombic prisms, belonging to the oblique prismatic system. Primary form (*Fig.* 81), with the faces *a*, *a* and *m*;—$u' : u = 90° 32'$; $m : i = 95° 46'$ (Mitscherlich, *comp.* Kupffer, *Pogg.* 2, 41, Bernhardi, *N. Tr.* 9, 2, 3.) Sp. gr. = 1·982. (Marchand & Scheerer.) According to the assertion of Breithaupt (*J. pr. Chem.* 4, 257), cited on page 98, Vol. I., the crystals *b* appear to be not only rather harder than the crystals *a*, but likewise to have a somewhat greater density. These crystals are pale brownish-yellow and perfectly transparent. In the course of a few days, at ordinary temperatures, they become opaque, pale yellow, and specifically heavier, assuming internally the structure of the crystals *a*, while externally they remain as pseudo-crystals of the form *b*. The slightest agitation, even blowing on the crystals, accelerates this change.

By cooling them as slowly as possible, and leaving them at perfect rest for 24 hours, they may be rendered more permanent. The change from *b* to *a* begins with the formation of isolated, bright yellow, opaque spots, which gradually spread themselves out. When the crystals have become perfectly opaque, their specific gravity is found to be increased from 1·982 to 2·038. The change is always accompanied by the formation of internal fissures. If, on the other hand, sulphur be kept for twelve hours at a temperature between 110° and 100°, its specific gravity diminishes from 2·049 to 1·985; but if it remain for several days at the ordinary temperature of the air, its density again rises to 2·048. If a thermometer be immersed in sulphur which is solidifying, and the cooling of the solid sulphur be retarded by surrounding it with cotton, slight blows on the side of the vessel will cause a rise of the thermometer of $\frac{1}{4}$° to 1°, and repeated blows a rise of 2° or 3°, inasmuch as the passage of the sulphur from *b* to *a* is attended with evolution of heat. But when once the sulphur has become perfectly opaque, no further rise of temperature is produced by agitation. (Marchand & Scheerer.) Rolled sulphur when newly cast is of the form *b*, but after a time changes to *a*. Flowers of sulphur when examined by the microscope present the appearance, not of crystals, but of smooth, opaque spherules of non-crystalline fracture. (Fritzsche.)

c. Soft, amorphous Sulphur. When sulphur is heated till it acquires a viscid consistence, and then poured into water kept as cold as possible, it becomes soft and of a reddish-brown colour, and acquires a density of 1·961: when it has become quite solid but is still coloured brown, the density is increased to 1·980; and when it has become quite yellow, to

2·041. (Marchand & Scheerer.) According to Osann, the specific gravity of *c* is 2·027. (*Vid.* I., 104.) Soft sulphur hardens in the course of 20 or 30 hours (Dumas), by transformation into *a*. The brown colour which characterizes the amorphous state may be heightened by the asphaltum which is often mixed with sulphur and is altered by the action of heat. The restoration of the yellow colour after a time is no objection to this view; for the opacity which the sulphur acquires at the same time prevents the brown colour from being perceived. Fourcroy and Thomson were of opinion that sulphur in the soft state is partially oxidized; but Irvine and Sir Humphry Davy have shown that the soft condition is produced equally well out of contact of air.

Sulphur melts at 104·5 (Berzelius), at 107° (Dumas), at 108°—109° (Dalton), at 111·75°—112° (Marchand & Scheerer), at 112·2° (Frankenheim. *J. pr. Chem.* 16, 7), and forms a brownish-yellow, transparent, thin, oily liquid, which, according to Osann (*Pogg.* 31, 33), has a specific gravity of 1·927. According to Knox, this liquid conducts the electric current of a sixty-pair battery. (See, on the contrary, p. 313., Vol. I.) Considerable masses of liquid sulphur solidify a few degrees below the melting point; smaller masses often remain liquid at ordinary temperatures. Sulphur begins to solidify between 109° and 108°. (Dumas.) During the process of solidification, the temperature falls to 99° or 100°, and rises again to between 109·4° and 110°. (Marx, *Schw.* 60, 1.) Considerable masses of melted sulphur may cool down to 108°, or even to 105° before solidifying; but as soon as solidification begins, the temperature rises to 112°, and remains there till the whole is solidified. (Frankenheim.) Solidification takes place at 111·5°: when it is completed, and the temperature of the sulphur has fallen somewhat below that point, it often rises suddenly again to 111·5°. (Marchand & Scheerer.) Sulphur in small drops often remains liquid at ordinary temperatures, and solidifies when touched with solid bodies. (I., 9; compare also Belleni, *N. Quart. J. of Sc.* 2, 469; Frankenheim, *J. pr. Chem.* 16, 7.) The minute drops deposited by the condensation of sulphur-vapour on a glass plate remain liquid for several days when left at rest, and finally solidify in the form of smooth globules: in this manner also flowers of sulphur are produced: but on agitation or exposure to light, the drops solidify in a few hours, spreading themselves out on the glass plate in the form of opaque hemispheres covered with crystalline points of the rhombic octohedral form. If the glass plate be wetted with oil, the crystals are larger and more quickly formed. (Fritzsche, *Pogg.* 42, 453.)

At a higher temperature, the melted sulphur loses its oily state and acquires a thick viscid consistence like turpentine: it likewise assumes a dark red-brown colour, and is no longer transparent, excepting in thin films. In this viscid state, the density of sulphur is, according to Osann, only 1·751. At 160°, sulphur begins to turn red and viscid; between 220° and 250°, it is so thick that it will not run out when the containing vessel is inverted; it also exhibits a red-brown colour. (Dumas.) Thickening begins at a temperature near 260°. When melted sulphur is heated, its temperature remains stationary for some time between 250° and 260°, but afterwards rises with proportionally greater quickness: on the other hand, sulphur heated above 260° cools down with tolerable regularity at first; but after the temperature has fallen to 260°, it suddenly becomes stationary for several minutes and oscillates within a few degrees above and below; after that, it falls regularly. Hence it appears that sulphur, in passing from the oily to the viscid state, renders heat

latent. (Frankenheim.) Results not in accordance with these have been obtained by Marx. (*Schw.* 60, 1.) When viscid sulphur is dropped into oil, it becomes covered with well developed crystals and loses its transparency. (Fritzsche.)

At still higher temperatures, up to the boiling point, sulphur again becomes more fluid, but not so much so as at 120°; it likewise acquires greater transparency, but retains a brown-red colour. The more fluid state commences at 207·5°, according to Osann, and at 250°, according to Dumas. When sulphur, by continued heating at a temperature of 300° has been wholly brought into the brown-red condition, and is then rapidly cooled, it exhibits a uniform decrease of temperature and does not pass through the intermediate viscid state; but if it be slowly cooled, it becomes viscid, the passage into this state being accompanied by a simultaneous interruption in the fall of temperature. (Frankenheim.) Sulphur fused at various temperatures and then quickly cooled in single drops by immersion in cold water behaves as follows: at 110°—170°, it solidifies to a yellow mass of the ordinary colour of sulphur. At 190°, it is at first soft and transparent, but soon becomes brittle and opaque, exhibiting the ordinary colour. At 220°, it becomes soft, transparent, and brownish-yellow. At 230°—260°, it becomes perfectly soft, ductile, transparent, and of a reddish colour. At the boiling point, very soft, transparent, and red-brown. Fusion for a long time has nothing to do with these conditions; all depends on the temperature. If the sulphur be poured into the water in large masses, the inner portions, which cool slowly, solidify in the form of ordinary sulphur. Rapid cooling prevents the crystallization. (Amorphism.) *Dumas.* The soft, plastic sulphur obtained by rapid cooling in water serves to take impressions of medals.

Sulphur boils at 293°, according to Davy, and at 440°, according to Dumas (*Ann. Chim. Phys.* 50, 175),—and is converted into an orange-coloured vapour, which has a faint and characteristic odour, and deposits small drops of sulphur on cold bodies.

Milk of Sulphur, Lac sulphuris. Sulphur separated in the cold, from aqueous solutions containing hydrosulphuric acid. To obtain it, prepare one of the following solutions: *a.* An aqueous solution of liver of sulphur. *b.* The solution *a* thoroughly saturated by boiling with sulphur. (Bucholz.) *c.* Sulphide of potassium, obtained by igniting sulphate of potassa with charcoal, then dissolved in water, and the solution saturated with sulphur at a boiling heat. (Bucholz.) *d.* Solution of caustic potash boiled with sulphur till saturated. *e.* One part of quicklime slaked with 3 parts water, and then boiled with 2 parts sulphur and 13 parts water. One of these liquids, after being left to stand for some days, then filtered and properly diluted with water, is precipitated by sulphuric, hydrochloric, or acetic acid free from metal. With *e*, only hydrochloric or acetic acid can be used. The acid must be added in small portions at a time, with constant stirring, to the sulphur solution, and in such quantity as not to decompose it completely; and the precipitate immediately collected on a filter and thoroughly washed. For the sulphur solutions, especially *d* and *e*, likewise contain alkaline hyposulphites, from which, if the acid be added in excess, or the mixture left to stand a long time, yellow sulphur is precipitated and becomes mixed with the milk of sulphur. (*Vid.* Wackenroder, *Br. Arch.* 26, 180.)

Milk of sulphur is a white powder with a tinge, not of yellow, but of grey—feels gritty between the fingers—and has a scarcely perceptible taste and odour.

That milk o sulphur is not, as asserted by Thomson, a hydrate of sulphur, has been shown by Bucholz (*Taschenb.* 1808, 135,) and Bischof (*Schw.* 43, 392). When thoroughly dried and then heated, it gives off, not water, but a small quantity of hydrosulphuric acid gas, and fuses together in the form of ordinary sulphur. (Berzelius, *Lehrb.* 1, 213.) Since this evolution of hydrosulphuric acid is constant, and cannot be prevented by previously washing the powder with water,—and since milk of sulphur is precipitated only from liquids which contain hydrosulphuric acid, Rose (*Pogg.* 47, 166) regards it as sulphur having hydrosulphuric acid, or rather persulphide of hydrogen, adhering to it. According to Osann (*Kastn. Arch.* 4, 344), it also contains 4 per cent. of carbon; but this is probably nothing but an accidental impurity.

Compounds of Sulphur.

Sulphur and Oxygen.

A. Hyposulphurous Acid. SO or S^2O^2.

Oxide of Sulphur, Sulphuretted Sulphurous acid, Dithionous acid, Unterschweflige Säure, Acide hyposulfureux, Acidum hyposulfurosum.

Formed, in combination with salifiable bases: 1. When certain metals, zinc for example, are dissolved in aqueous sulphurous acid. 2 atoms of zinc with 3 atoms of sulphurous acid form 1 atom of sulphite and 1 atom of hyposulphite of zinc:

$$2Zn + 3SO^2 = ZnO, SO^2 + ZnO, S^2O^2.$$

(Mitscherlich, *Pogg.* 8, 442.)—2. When an aqueous solution of an alkaline sulphite is boiled with sulphur, the sulphur being dissolved in considerable quantity:

$$(KO, SO^2 + S = KO, S^2O^2)$$

3. When the solution of an alkaline sulphite is decomposed by a small quantity of hydrosulphuric acid, or of the sulphide of an alkali-metal. With hydrosulphuric acid the decomposition is probably—

$$2KO, 2SO^2 + HS = 2KO, 3SO + HO.$$

and with sulphide of potassium—

$$2KO, 2SO^2 + KS = 3KO, 3SO.$$

4. When the solution of the sulphide of an alkali-metal is mixed with sulphurous acid. (Vauquelin.) In this case, sulphur and hydrosulphuric acid are set free, and a small quantity of an alkaline sulphite is formed together with the hyposulphite. (Mitscherlich, *Pogg.* 8, 441.)—5. When the solution of a poly-sulphide of an alkali-metal is exposed to the air—

$$KS^2 + 3O = KO, S^2O^2.$$

6. When sulphur is fused at a gentle heat with an alkaline hydrate, or boiled with an aqueous solution of the alkali. In this case, a pentasulphide of the metal is formed at the same time.

$$3KO + 12S = KO, S^2O^2 + 2KS^5.$$

7. When aqueous solutions of various alkaline salts, saturated with hydrosulphuric acid, are heated to the boiling point in contact with the air. Borax, chlorate, neutral tartrate, and acetate of potassa, phosphate and acetate of soda, and acetate of baryta, treated in this manner, yield small quantities of alkaline hyposulphites; sulphate and nitrate of potassa, and sulphate of soda yield but a trace. (L. A. Buchner, *Repert.* 61, 36.)

Calculation.			Or:			Or:		
S	16	66·67	2S	32	66·67	S	16	33·33
O	8	33·33	2O	16	33·33	SO^2	32	66·67
SO	24	100·00	S^2O^2	48	100·00	S^2O^2	48	100·00

(S^2O^2 = 2 . 201·17 + 2 . 100 = 602·34. Berzelius.)

This acid is not known in the free state, on account of its tendency, when separated from its combinations, to resolve itself into sulphurous acid and sulphur. ($S^2O^2 = SO^2 + S$.) When an alkaline hyposulphite, dissolved in water, is decomposed by the action of a stronger acid, the liquid, according to Herschel, acquires a harsh, sour, and very bitter taste, and the property of precipitating metallic sulphides from solutions of nitrate of mercurous oxide and nitrate of silver: it exerts no immediate action upon salts of zinc, iron, and copper; but in a few seconds, especially if heat be applied, half of the sulphur is precipitated, and the other half remains in the liquid, combined with the whole of the oxygen in the form of sulphurous acid. According to H. Rose, a very small quantity of the acid remains undecomposed for several weeks. The cause of the decomposition may be, that water has a much greater affinity for sulphurous than for hyposulphurous acid. It must, however, be observed, that when anhydrous hyposulphite of strontia is decomposed by hydrochloric acid gas, or by alcohol saturated with that gas (in which case, only a small quantity of water can be formed from the oxygen of the strontia and the hydrogen of the hydrochloric acid), the acid which is set free is resolved into sulphurous acid and sulphur. (Gay-Lussac.) Also, when hyposulphite of lead diffused through water at 0° is decomposed by hydrosulphuric or sulphuric acid, an aqueous solution of hyposulphurous acid is at first obtained, but that acid is quickly resolved into sulphurous acid and sulphur. (Pelouze.) Sulphur precipitated from aqueous solutions of alkaline hyposulphites on the addition of an acid, takes the form, not of milk of sulphur, but of plastic sulphur, forming globules of different magnitudes, which remain soft for a long time under water, but become crystalline when exposed to the air or placed in contact with fixed oils.

Hyposulphurous acid in combination with salifiable bases forms salts called *Hyposulphites, Dithionites, Sulphuretted Sulphites, Salts of Sulphuric Oxide, Unterschwefligsauren Salze.* For their formation and preparation, *vid.* p. 160. They generally contain one atom of acid, S^2O^2, combined with one atom of base. They appear to be unable to exist without at least one atom of water. (H. Rose, *Pogg.* 21, 439.) The alkaline hyposulphites, when heated out of contact of air, are resolved into water, sulphur, and hydrosulphuric acid, which escape, and a mixture of a metallic sulphide with an alkaline sulphate, the proportions of which vary according to the temperature. (H. Rose.) When thrown into nitre in a state of fusion, they evolve red vapours. (H. Rose.) Boiled with water and sulphur, they decompose the water, evolve hydrosulphuric acid, and form a sulphate of the base. (Pelouze, *Ann.*

Chim. Phys. 79, 86.) The aqueous solution of an alkaline hyposulphite remains unaltered in the air, according to Gay-Lussac; but if the salt contains more than one atom of alkali for each atom of S^2O^2, it is converted first into a sulphite, and then into a sulphate.

$$KO, S^2O^2 + KO + 4O = 2KO, 2SO^3.$$

When digested in nitric acid till the sulphur which is precipitated at first is re-oxidized and dissolved, they yield two atoms of sulphuric acid for each atom of alkali. (Gay-Lussac.)

$$KO, S^2O^2 + 4O = KO + 2SO^3.$$

Stronger acids, even sulphurous acid, decompose the hyposulphites, the acid of which is then resolved into sulphurous acid and sulphur. Hydrochloric acid separates sulphurous acid, with effervescence, from the fixed hyposulphites. All alkaline hyposulphites are soluble in water, the baryta-salt, however, but slightly. The solutions give the following reactions: With *protochloride of tin dissolved in aqueous hydrochloric acid:* An immediate brown precipitate, even when the quantity of alkaline hyposulphite is very small. (H. Rose.) *Lead-salts:* White precipitate; turning black even below 100°. (Herschel.) *Solution of protochloride of copper,* in the cold: White precipitate of dichloride of copper. *Oxygen-salts of protoxide of copper,* in the cold: Nothing, at first; turbidity after some time. *All proto-salts of copper,* at a boiling heat: Black precipitate of sulphide of copper, free sulphuric acid remaining in the liquid.

$$CuO, S^2O^2 = CuS, SO^3. \quad \text{(H. Rose.)}$$

(According to Pfaff, *Schw.* 44, 490), proto-salts of copper give a yellow-green precipitate, which after a time becomes red-brown.) *Nitrate of mercurous oxide:* Immediate black precipitate. (H. Rose.) *Protochloride of mercury* and *oxygen-salts of mercuric oxide not in excess:* White precipitate of mercuric hyposulphite, which turns first yellow, then brown, and is ultimately converted into black sulphide of mercury—the change taking place very rapidly at a boiling heat—while free sulphuric acid remains in the liquid. The same mercuric salts used in excess: White precipitate, which settles down slowly, remains white even on boiling, and consists of a compound of sulphide of mercury with the protochloride, or with an oxygen-salt of mercuric oxide; the supernatant liquid contains free sulphuric acid. (H. Rose.) According to Wackenroder and L. A. Buchner (*Repert.* 61, 24), on the contrary, nitrate of mercuric oxide gives a copious, lemon-yellow floculent precipitate, which when the mercuric salt is in excess, becomes yellowish-white. *Nitrate of silver:* White precipitate, which becomes first yellow, then brown, and is finally converted into black sulphide of silver—the change being greatly accelerated by heat—while free sulphuric acid remains in the liquid. (Herschel; H. Rose.) The alkaline hyposulphites dissolve freshly precipitated chloride of silver.

¶ B. Pentathionic Acid. S^5O^5.

Tersulphuretted Hyposulphuric acid, Tersul-hyposulphuric acid.

Formation. 1. By the mutual action of sulphurous and hydrosulphuric acid:—5 atoms of sulphurous acid and 5 atoms of hydrosulphuric acid, react upon one another in such a manner as to form 1 atom of pen-

tathionic acid, 5 atoms of water, and 5 atoms of sulphur, which separate in the solid state. (Wackenroder.)

$$5SO^2 + 5HS = S^5O^5 + 5HO + 5S.$$

2. By the action of aqueous solution of sulphurous acid on chloride of sulphur.

This acid is not known to exist in the separate state.

	Calculation.		Lenoir.	Or:	Calculation.	
5S	80	66·67	66·67	S^2O^5	72	60
5O	40	33·33	33·33	S^3	48	40
S^5O^5	120	100·00	100·00	S^5O^5	120	100

(S^5O^5 = 5 . 201·17 + 5 . 100 = 1505·85. Berzelius.)

Combinations. *a.* With Water. *Hydrated Pentathionic acid.* (1.) Wackenroder passes sulphuretted hydrogen in excess through a saturated solution of sulphurous acid in water—filters and digests the milky filtrate with slips of clean metallic copper, till it becomes clear—filters again—removes the dissolved copper by sulphuretted hydrogen—and drives off the excess of the latter by the application of a gentle heat. The solution thus obtained is colourless and destitute of odour; it may be concentrated without decomposition till it attains the specific gravity of 1·37.—(2.) Kessler passes sulphurous and hydrosulphuric acid gases alternately through water, till the precipitated sulphur forms a thick magma at the bottom of the vessel—digests the filtered liquid with freshly precipitated carbonate of baryta, to remove sulphuric acid—filters, and concentrates the filtrate over a water-bath, till it attains a density of 1·25—1·3. The acid liquid thus obtained may be further concentrated in vacuo, to the density of 1·6 at the temperature of 22° (71·6° F.).

Hydrated pentathionic acid is colourless and inodorous, and has a strongly acid taste, inclining to bitter. It may be preserved unchanged at the temperature of the air; but on attempting to concentrate it by heating beyond the density of 1·37, it is decomposed, sulphuretted hydrogen, and afterwards sulphurous acid being evolved, while sulphuric acid and sulphur remain behind. It is not decomposed by sulphuretted hydrogen, or by dilute hydrochloric or sulphuric acid; the latter, however, when concentrated decomposes it. By nitric acid, hypochlorous acid, or chlorine, it is oxidated and converted into sulphuric acid. Metallic copper and iron decompose it at a boiling heat, the former with evolution of sulphurous acid and formation of sulphide of copper; the latter with evolution, first of sulphuretted hydrogen, then of sulphurous acid, a portion of the latter also remaining in the liquid. (Wackenroder.) A moderately concentrated solution of pentathionic acid gives off a faint sulphurous smell when boiled, but does not evolve sulphurous acid gas except when highly concentrated; on boiling it with hydrochloric acid, the odour of sulphuretted hydrogen is perceptible. On boiling the acid with solution of caustic potash, hyposulphite and sulphate of potassa, and sulphide of potassium are formed. ($S^5O^5 = SO^3 + S^2O^2 + 2S.$) (Kessler.)

Sulphate of copper added to a solution of pentathionic acid produces a brown precipitate after long boiling. *Nitrate of mercurous oxide* gives a yellow precipitate which slowly blackens on boiling;—*Chloride of mercury:* by degrees, a yellowish precipitate, consisting of a compound of sulphide and chloride of mercury mixed with free sulphur;—*Cyanide of mercury:* by degrees, a yellow precipitate which blackens slowly in the cold, imme-

diately on boiling;—*Nitrate of silver*: a yellow precipitate, which soon turns black. When a solution of pentathionic acid is rapidly mixed with excess of ammonia, the addition of an ammoniacal solution of nitrate of silver quickly produces a brown colour, which gradually becomes darker, while sulphide of silver separates from the liquid. An ammoniacal solution of chloride of mercury added to the same liquid gradually produces a black precipitate of sulphide of mercury; and on the addition of hydrosulphuric acid, a separation of sulphur takes place. (Kessler.)

b. With Salifiable Bases. The salts of this acid, the *Pentathionates*, have not been much examined. They are very instable,—so much so, that it is difficult to obtain them in the solid state. In fact, the fifth atom of sulphur in the acid appears to be retained by only a feeble affinity; and in presence of a strong base, especially if the solution be concentrated, this last atom of sulphur is separated, and the result is the formation of tetrathionic acid, the salts of which have greater stability. Sometimes two atoms of sulphur are given up and trithionic acid (S^3O^5) is produced. Kessler found that on mixing solution of pentathionic acid of specific gravity 1·32 (prepared by either of the methods above described) with solution of acetate of potassa in alcohol of 96 per cent., washing the precipitate with alcohol, and dissolving it in warm water, a considerable quantity of sulphur remained undissolved, and the solution mixed with alcohol yielded crystals having the form and composition of tetrathionate of potassa, KO, S^4O^5. The pentathionates of baryta and lead are soluble in water, but cannot be obtained in the solid state by evaporation even in vacuo, decomposition taking place as soon as the solutions attain a certain degree of concentration. Lenoir, however, obtained the baryta salt in definite crystals by mixing the freshly prepared aqueous solution with strong alcohol. The salt then separated abundantly in transparent silky prisms which changed within the liquid to larger and well-defined crystals. These crystals were analysed, and found to consist of BaO, S^5O^5, HO. This determines the composition of the acid, and shows it to be isomeric (or rather, polymeric) with hyposulphurous acid.

¶ C. Tetrathionic Acid. S^4O^5.

Bisulphuretted Hyposulphuric acid, Bisul-hyposulphuric acid.

Formation. 1. By the action of iodine on solutions of the hyposulphites, that of soda, for example, 2 At. hyposulphite of soda and 1 At. iodine producing 1 At. iodine of sodium and 1 At. tetrathionate of soda.

$$2\,(NaO, SO^2) + I = NaI + NaO, S^4O^5.$$

2. By the decomposition of pentathionic acid (see above). Fordos & Gélis, in examining the action of aqueous solution of sulphurous acid on chloride of sulphur, were at first led to suppose that both tetrathionic and trithionic acid were thereby produced; but they afterwards found that these two acids were not formed at first—but, at a later period, by the decomposition of the pentathionic acid produced in the first instance: hence they concluded that pentathionic acid is the only acid of the series produced by the direct action of aqueous sulphurous acid on chloride of sulphur.

Tetrathionic acid has not been obtained in the separate state: its composition is as follows:—

Calculation.			Or:	Calculation.	
4S	64	61·54	S^3O^5	72	69·23
5O	40	38·46	S^2	32	30·77
S^4O^5	104	100·00	100	104	100·00

$S^4O^5 = 4 . 201{\cdot}17 + 5 . 100 = 1304{\cdot}68$. Berzelius.)

Combinations. a. With Water. *Hydrated Tetrathionic acid.* (1.) When hyposulphite of baryta is dissolved in a very small quantity of water, and iodine added in successive portions to the solution, iodide of barium and tetrathionate of baryta are formed, and both dissolve in the water. The latter, however, is soon deposited in flakes which continually increase in abundance, inasmuch as the quantity of water present is not sufficient to dissolve the whole of the salt. Complete saturation having been attained, the magma of crystals is digested in strong alcohol, which dissolves the iodide of barium and excess of iodine, but leaves the tetrathionate of baryta undissolved in the form of a white powder; and by dissolving this powder in a very small quantity of water and leaving the solution to spontaneous evaporation, the salt is obtained in beautiful crystals: the addition of a little alcohol facilitates the crystallization. The salt thus obtained being dissolved in water, sulphuric acid added to the solution in quantity just sufficient to precipitate the baryta, and the liquid filtered, a solution of tetrathionic is obtained which may be concentrated to a considerable extent by evaporation. (Fordos & Gélis, *Compt. Rend.* 15, 920.) (2.) Kessler finds that the acid obtained by the preceding process is never absolutely pure, because tetrathionic acid, by contact with strong bases, such as baryta, is resolved, more or less, into trithionic acid and sulphur ($S^4O^5 = S^3O^5 + S$). To avoid this source of impurity, Kessler prepares the acid from the lead salt. This he obtains by pouring a warm dilute solution of 2 parts of hyposulphite of soda, into a solution of 3 parts of acetate of lead, likewise warm and dilute —washing the precipitate, and mixing it while yet moist with 1 part of iodine: in a few days, the whole is converted into iodide of lead and solution of tetrathionate of lead perfectly free from trithionic acid. The lead being precipitated from this solution by sulphuric acid, and the excess of that acid removed by digestion with carbonate of baryta, a pure solution of tetrathionic acid is obtained, which may be evaporated over the water-bath to a small bulk.

The solution of tetrathionic acid is colourless and transparent; has about the same degree of stability as hyposulphuric acid: by boiling, it is resolved into sulphur, sulphurous acid, and sulphuric acid: hydrochloric and sulphuric acid do not decompose it, but nitric acid causes a precipitation of sulphur. (Fordos & Gélis.) According to Kessler, on the contrary, it is not decomposed by boiling, but evolve ssulphuretted hydrogen when mixed with hydrochloric acid and gently warmed. (The acid examined by Fordos & Gélis probably contained trithionic acid.) When boiled with solution of caustic potash, it is converted into hyposulphite and sulphate of potassa, together with sulphide of potassium:

$$S^4O^5 = SO^3 + S^2O^2 + S. \text{ (*Kessler.*)}$$

Tetrathionic acid resembles pentathionic acid in its behaviour with solutions of sulphate of copper, nitrate of mercurous oxide, chloride of mercury, cyanide of mercury, and nitrate of silver; but is distinguished from

pentathionic acid by its behaviour with an ammoniacal solution of silver. When tetrathionic acid is supersaturated in the cold with ammonia, no alteration is produced in it by the addition of ammoniacal solution of nitrate of silver, or cyanide of mercury, or finally by sulphuretted hydrogen. (For the corresponding reactions of pentathionic acid, *vid.* pp. 163, 164.)

b. With Salifiable Bases. *Tetrathionates.* These salts are much more stable than the pentathionates: several of them have been obtained in the solid state, and will be described hereafter. The acid is however liable, especially when in contact with a strong base, to resolve itself into trithionic acid and sulphur; and the salts are particularly prone to this decomposition when their aqueous solutions are concentrated by evaporation. The best mode of obtaining them in the crystalline state is to mix the aqueous solutions with strong alcohol. In this manner the salts of potassa, baryta, strontia and lead have been obtained in well-defined crystals. ¶

D. Trithionic Acid. S^3O^5.

Sulphuretted Hyposulphuric acid, Monosul-hyposulphuric acid, Acide hyposulfurique sulfuré, Niederschwefelsäure.

Formation. 1. By gently heating an aqueous solution of bisulphite of potassa with sulphur. (*Vid. seq.*)—2. By the decomposition of pentathionic and tetrathionic acid. (p. 164).

Not known in the free state.

According to Langlois.			Or:	Calculation.		Or:	Calculation.		Or:	Calculation.	
3S	48	54·55	SO	24	27·27	S^2O^2	48	54·55	S	16	18·18
5O	40	45·45	$2SO^2$	64	72·73	SO^3	40	45·45	S^2O^5.	72	81·82
S^3O^5.	88	100·00	S^3O^5....	88	100·00	S^3O^5	88	100·00	S^3O^5	88	100·00

(S^3O^5 = 3.201·17 + 5.100 = 1103·51. Berzelius.)

The reactions of this acid favour the supposition that it is a compound of hyposulphurous and sulphuric acid (S^2O^2, SO^3).

Combinations. a. With Water. *Aqueous Trithionic acid.*

Preparation. A saturated solution of bisulphite of potassa is heated with flowers of sulphur in a flask for three or four days, till the yellow colour which the liquid first assumes has disappeared. The heat must not be raised to the boiling point, for the compound would then be destroyed. Sulphurous acid is evolved and trithionate of potassa is formed together with small quantities of sulphate and hyposulphite. The solution filtered hot becomes turbid on cooling from deposition of sulphur, and yields crystals of trithionate of potassa mixed with sulphur and with a small quantity of sulphate: they may be obtained in a state of purity by dissolving them in the smallest possible quantity of tepid water, then filtering and cooling the solution. (Langlois.) According to Pelouze, the simultaneous formation of hyposulphite of potassa is essential to the process,—but that of sulphate takes place merely in consequence of the heat becoming too great, whereby the trithionate of potassa is decomposed. According to this view, the process may be represented by the following equation:—

$$3\,(KO, 2SO^2) + 2S = 2\,(KO, S^3O^5) + (KO, S^2O^2.)$$

On saturating cold water with the potash-salt thus obtained—adding to the solution, in small portions at a time, the quantity of tartaric, or better, of perchloric acid required to precipitate the base—and filtering, the acid is obtained in the state of aqueous solution. This solution may be concentrated by evaporation at a gentle heat, or with greater security, in vacuo over oil of vitriol; but it is thereby rendered more liable to decomposition. (Langlois.)

The aqueous solution of trithionic acid is a transparent and colourless liquid, of somewhat syrupy consistence when highly concentrated; not very corrosive, inodorous, and of a sour and somewhat harsh and bitter taste. (Langlois.)

It is perfectly pure only when newly prepared, being resolved, gradually at ordinary temperatures, and quickly at 80°, into sulphur which precipitates, sulphurous acid which escapes as gas, and sulphuric acid which remains in solution. Only the dilute solution can be preserved. By nitric acid, it is immediately converted into sulphuric acid, with evolution of nitric oxide and precipitation of sulphur. Chloric acid also converts it into sulphuric acid, with separation of sulphur and chlorine. Iodic acid exerts a similar action. Perchloric and hydrochloric acids have no effect upon it, and oil of vitriol decomposes it merely in consequence of the rise of temperature which it occasions. (Langlois.)

¶ When this acid is boiled with caustic potash, hyposulphite and sulphate of potassa are formed, but no sulphide of potassium ($S^3O^5 = SO^3 + S^2O^2$); the addition of acetate of lead does not give a black precipitate. *Sulphate of copper* in excess decomposes the acid completely, on boiling, a precipitate of sulphide of copper being formed. *Nitrate of mercurous oxide* gives a black precipitate of disulphide of mercury; *Chloride of mercury*, a perfectly white precipitate which is a compound of sulphide and chloride of mercury without free sulphur; *Cyanide of mercury* gradually forms a yellow precipitate blackening slowly in the cold, rapidly on boiling; *Nitrate of silver*, a perfectly white precipitate which quickly blackens. With ammoniacal solutions of nitrate of silver or cyanide of mercury trithionic acid behaves just like tetrathionic acid (p. 166, Kessler). Its behaviour with potassa, sulphate of copper, nitrate of mercurous oxide, chloride of mercury, and nitrate of silver distinguishes it both from pentathionic and from tetrathionic acid: from the former it is likewise distinguished by its behaviour with ammoniacal solution of silver or of cyanide of mercury. ¶

b. With Salifiable Bases. Among the *Trithionates*, the potash-salt is the only one that is known with any degree of accuracy. It is decomposed at a red heat into one atom of sulphur, one atom of sulphurous acid, and one atom of sulphate of potassa. (Langlois.)

$$KO, S^3O^5 = KO, SO^3 + SO^2 + S.$$

Its solution is resolved on boiling into sulphate of potassa, sulphurous acid, and sulphur. (Pelouze.) In the circuit of the voltaic battery, it yields bisulphate of potassa at the positive pole. Chlorine gas passed through this solution converts the acid into sulphuric acid. Nitrate acid acts violently upon it, evolving nitric oxide and precipitating sulphur. Oil of vitriol added to it causes a rise of temperature, precipitating sulphur and evolving sulphurous acid. This salt is not decomposed by hydrochloric acid, even when concentrated, nor by chloric or iodic acid. The aqueous solution of the potash-salt decolorizes sulphate of manganic oxide, but does not at ordinary temperatures precipitate the salts of baryta, strontia, lime, magnesia, alumina, uranic oxide, oxide of lead, oxide of zinc, or of the

protoxides of cobalt, nickel, and copper. It decomposes baryta-salts on the application of heat, sulphate of baryta being formed. (Pelouze.) With mercurous salts it gives a black precipitate of sulphide of mercury; with mercuric salts a white precipitate of sulphate of mercurous oxide; and with nitrate of silver a yellowish-white precipitate, which quickly turns black, in consequence of the formation of sulphide of silver. (Langlois.) ¶ Trithionate of baryta is obtained in shining laminæ by saturating the acid with carbonate of baryta, and adding alcohol to the liquid. The solution of this salt is easily decomposed, with separation of sulphate of baryta. The crystals are composed of $BaO, S^3O^5 + 2HO$. ¶

At the commencement of his investigation of trithionic acid, and before he had convinced himself of its peculiar nature, Langlois thought that he was dealing with hyposulphurous acid. At the same time, Persoz (*J. Chem. Med.* 16, 383) was endeavouring to isolate hyposulphurous acid. His process was as follows:—He precipitated the potash-salt (the mode of preparing it is not given) by nitrate of lead, washed the precipitate, diffused it through water, decomposed it with hydrosulphuric acid, and evaporated the filtrate, which deposited but little sulphur, either by a gentle heat or in vacuo. In this manner, he obtained a transparent colourless liquid, which reddened litmus strongly, and had a density of about 2·000. When heated, it was resolved into sulphuric acid and sulphur. It was oxidized, with separation of sulphur, by nitric, chloric, and hypochlorous acids; it was also decomposed by oil of vitriol, with precipitation of sulphur, and precipitated protosulphide of tin from an aqueous solution of the protochloride, on the application of heat. The acid of Persoz is perhaps also trithionic acid: but trithionate of potassa does not precipitate lead-salts. Can it be that hyposulphite of lead was first precipitated, and that trithionic acid was formed from it by the subsequent treatment?

¶ The three acids just described are included under the general name of *Polythionic acids*, from their containing more than one atom of sulphur. The hyposulphurous and hyposulphuric acids, S^2O^2 and S^2O^5, properly belong to the same series, and may be included in it with the respective appellations of *Dithionous* and *Dithionic* acid; but the names by which they have hitherto been distinguished are too well established to be easily laid aside. Two other acids, having the formulæ S^5O^6 and S^6O^7, were also asserted by Plessy (*N. Ann. Chim. Phys.* 20, 162) to be formed by the action of hydrated sulphurous acid on the chlorides of sulphur; but Fordos & Gélis have shown that these supposed new acids are merely mixtures of the different acids of the polythionic series above described. ¶

E. Sulphurous Acid. SO^2.

Imperfect Sulphuric acid; Volatile, phlogisticated Vitriolic acid; Schwefflige Säure, Acide sulfureux, Acidum sulfurosum, Acidum Vitrioli phlogisticatum;—and in the gaseous state: *Sulphurous acid gas, Sulphuric acid gas, Vitriolated air, Schwefligsaures, Schwefelsaures Gas, Vitriolsaure Luft, Gas acide sulfureux, Gas acidum sulphurosum.*

Occurrence in nature. In the neighbourhood of volcanos, both in the gaseous state, and in springs.

Formation. 1. In the burning of sulphur. Sulphur takes fire at 260°, according to Dalton, at 294°, according to Thomson, and burns with a blue flame in air, but with a brilliant violet flame in oxygen gas. The oxygen consumed is replaced by sulphurous acid gas occupying almost exactly the same volume. (H. Davy.)—2. When sulphur is heated with the oxides of manganese, zinc, lead, mercury, and other metals.—3. On bringing chloride of sulphur in contact with water.—4. In the decomposition of hyposulphurous, pentathionic, tetrathionic, and trithionic acid.—5. In the decomposition of hyposulphuric acid by heat.—6. On heating concentrated sulphuric acid with many metals, or with charcoal or organic substances.

Preparation of the Gas. 1. Oil of vitriol is heated with one-third of its weight of copper, or its own weight of mercury, till the mass becomes solid. (*Scheme* 23.) The gas must be passed through a Woulfe's bottle containing water, in order to arrest sulphuric acid, mercury, &c., which may be carried over with it.—2. By heating oil of vitriol with charcoal or wood-shavings: *e. g.*, according to Knezaurek, a stiff mixture of oil of vitriol and charcoal powder.—The gas prepared by this method is contaminated with carbonic acid.—3. By heating 1 part of sulphur with 7 or 8 parts of manganese. (Berthier.) The gas thus obtained is mixed with sulphur-vapour, oxygen gas, and frequently also with carbonic acid gas. (Marchand.)—4. A mixture of 1 part sulphur and 3 parts black oxide of copper is placed in a tube and covered with a layer of pure oxide; the latter is then heated first, and afterwards the mixture. (Marchand. *Pogg.* 42, 144.)—5. By burning sulphur in the air. For this purpose, Brunner's aspirator (II. 34) may be used. The sulphurous acid thus produced is mixed with the nitrogen of the air and a small quantity of oxygen. The first and fourth methods yield the purest gas. The gas is collected over mercury. If it be wanted free from moisture, it must be previously passed through a tube filled with chloride of calcium.

Preparation of the Liquid Acid. 1. Faraday pumps the dry gas into a tube previously exhausted of air and cooled, till a pressure of 3 to 5 atmospheres is attained.—2. Bussy passes the gas, prepared in the flask *a* (*App.* 45), by method 1, first through a Woulfe's bottle *b* surrounded with ice, in which the greater part of the watery vapour is condensed—then through a chloride of calcium tube *c*, by which the rest of the moisture is retained—aud lastly into a small Woulfe's bottle *d*, surrounded with a freezing mixture consisting of equal weights of ice and salt, and fitted with a bent tube which serves to convey the air of the apparatus and the uncondensed gas under mercury.—3. Wach (*Schw.* 50, 26) distils in a long glass tube sealed at both ends and somewhat bent, a mixture of 1 part sulphur and 5 parts anhydrous sulphuric acid, applying a very gentle heat to the arm of the tube containing the materials, and keeping the empty arm cool by means of a freezing mixture; the acid which passes over must be several times poured back again to free it from sulphuric acid. Bussy's method is the most convenient. The acid is preserved either in strong well-stopped bottles at the temperature of 0°, or else in sealed tubes.

Preparation of the Solid acid. 1. Bussy brings the liquid acid to rapid evaporation under the exhausted receiver of the air-pump. Part of it solidifies in the form of white flakes.—2. Mitchell (*Ann. Pharm.* 37, 356) surrounds the vessel containing the liquid acid with a mixture of solid carbonic acid and ether.

Properties of Solid Sulphurous acid. Forms white flakes. (Bussy.) Specifically heavier than the liquid acid. Freezing point about —79° C., or —110° Fah. (Mitchell.)

Properties of the liquid acid. Colourless, transparent, very thin liquid. Sp. gr. 1·42° (Faraday), 1·45° (Bussy). Refractive power about equal to that of water (Faraday), or somewhat greater. (De la Rive.) Boils at —10° C. (+ 14° F.) under the ordinary pressure of the atmosphere (Faraday), and at —10·5° (+ 13·1° F.) under a pressure of 29·3 inches. (Bunsen.) This liquid in passing into the state of gas, produces intense cold, thereby cooling itself in a short time below its own boiling point, so that afterwards the vaporization goes on more slowly. It freezes water on which it is poured.

Properties of the Gas. Refracting power, tension, and specific gravity (I., 95, 261 and 279). Colourless, incombustible, not capable of supporting the combustion of other bodies; of pungent, suffocating odour; wholly irrespirable; reddens litmus, and decolorizes roses, violets, paper dyed with logwood, &c., provided water is present.

	Calculation.		Berzelius.	Thomson.	Clem. & Desormes.
S	16	50	49·968	53	59
2O	16	50	50·032	47	41
SO^2	32	100	100·000	100	100

	Vol.	Sp. gr.		Vol.	Sp. gr.
Sulphur vapour	1	6·6556	=	⅙	1·1093
Oxygen gas	6	6·6558	=	1	1·1093
Sulphurous acid gas	6	13·3114	=	1	2·2186

(SO^2 = 201·17 + 2 . 100 = 401·17. Berzelius.)

Decompositions. 1. The liquid acid does not conduct the electricity of a forty-pair battery; but on the addition of water, it yields sulphur at the positive and hydrogen at the negative pole. (De la Rive.) The liquid acid (quite dry?) conducts the electricity of a 250-pair battery as well as a metal, and evolves oxygen at the positive pole, whilst at the negative pole nothing appears at first, but subsequently sulphur is deposited. (Kemp, *N. Ed. J. of Nat. and Geograph. Sc.* 1, 27.)—2. When the gas in a moist state is passed through a red-hot tube, it is resolved into sulphur and concentrated sulphuric acid. (Priestley; Berthollet.)—3. When hydrogen gas and sulphurous acid gas are passed together through a red-hot tube, water is formed and sulphur deposited; and when sulphurous acid gas is passed through a tube containing ignited charcoal, carbonic acid is produced and sulphur precipitated. Phosphorus gently heated does not decompose sulphurous acid gas. (Fourcroy & Vauquelin.) Phosphorus kept for some weeks in a solution of sulphurous acid acquires a bright yellow coating. (Vogel, Junr. *J. pr. Chem.* 19, 294.)—4. With phosphuretted hydrogen at ordinary temperatures, sulphurous acid gas forms water and sulphide of phosphorus; similarly with hydrosulphuric acid gas, it yields water and sulphur; with hydriodic acid gas, water, sulphur, and iodine; and with hydrochloric acid gas, water, sulphur, and chlorine. Aqueous phosphorous acid heated with aqueous sulphurous acid yields phosphoric and hydrosulphuric acid:

$$3PO^3 + 2SO^2 + 2HO = 3PO^5 + 2HS;$$

and the hydrosulphuric acid thus formed acts upon the excess of sulphurous acid in such a manner as to form water and sulphur. (Wöhler,

Ann. Pharm. 39, 252.) 6. Many metals heated in sulphurous acid gas are converted—sometimes with evolution of light and heat—into metallic oxides and sulphides. Many metals, as zinc, tin, and iron, abstract oxygen from aqueous sulphurous acid and convert it into hyposulphurous acid: *e. g.*

$$2Zn + 3SO^2 = ZnO, S^2O^2 + ZnO, SO^3.$$

When copper is immersed in the aqueous acid at ordinary temperatures and out of contact of air, sulphide and sulphate of copper are formed. (Baruel, Junr. *J. Pharm.* 20, 17.)

$$2Cu + 2SO^2 = CuS + CuO, SO^3.$$

Zinc immersed in an aqueous solution of sulphurous acid mixed with dilute sulphuric or hydrochloric acid causes an evolution of hydrosulphuric acid gas; and this, when the quantity of sulphurous acid present is considerable, may give rise to precipitation of sulphur.

$$3ZnO + SO^2 + HO + 3SO^3 = 3\,(ZnO, SO^3) + HS.$$

(Fordos & Gélis, *J. Pharm.* 27, 730.) See also Köne (*Pogg.* 63, 245), Fordos & Gélis *J. pr. Chem.* 31, 402), Muspratt (*Ann. Pharm.* 56, 259).

Combinations. *a.* With Water. *α. Crystallized Sulphurous acid.* Produced in the form of delicate white laminæ when sulphurous acid gas not perfectly dry is cooled by means of a freezing mixture—and likewise as a white snow-like mass when the liquid acid evaporates in the air. Contains about 20 pts. acid and 80 pts. water. Remains solid till raised to between 4° and 5° C. (40° and 41° F.); but above that temperature it melts, water being formed, with evolution of sulphurous acid gas. (De la Rive.)

¶ Pierre (*N. Ann. Chim. Phys.* 23, 416) has obtained the crystallized hydrate just mentioned by passing vapour of water, together with a large excess of sulphurous acid gas, through a tube cooled to between − 6° and − 8° C. The crystals were produced in abundance, but they were confused and opaque. They were found to contain $SO^2, 11HO$. But as these crystals had been formed at a temperature a few degrees below 0°, it seemed probable that crystals of ice might be associated with them; indeed their appearance was in favour of this supposition. To obviate this source of inaccuracy, Pierre endeavoured to form the crystals by exposing a highly concentrated aqueous solution of sulphurous acid for some time to a temperature of 0°. Groups of crystals were formed, the primary form of which appeared to be an oblique, rhombic prism. These crystals fused at 4°, evolving sulphurous acid. When thrown upon a platinum dish heated to between 20° and 25°, they made a hissing noise like water thrown upon a surface at a dull-red heat. Their composition was found to be:

	Calculated.	Found.	
SO^2	28·35	27·85	28·01
9HO	71·65	72·15	71·99

Similar results have been obtained by Döpping. (*J. pr. Chem.* 44, 255.) ¶

β. Aqueous solution of Sulphurous acid, otherwise called *Spiritus Sulphuris per Campanum.* When liquid sulphurous acid is cautiously poured into ice-cold water, it settles at the bottom and forms a distinct stratum; but if a rod be then immersed in the liquids so as to disturb them, combination takes place, attended with so great an evolution of

heat, (which is further increased by the water giving up its latent heat and being converted into ice,) that the liquid boils violently and gas is evolved. (Bussy.) By contact with a piece of ice also, sulphurous acid is instantly brought to a state of ebullition. (Faraday.) According to Fourcroy & Vauquelin (*Crell. Ann.* 1800, 2, 307), water at 5° absorbs one-seventh of its weight of sulphurous acid, and the specific gravity of the solution is 1·020. According to Priestley, the quantity of the gas absorbed by water at ordinary temperatures is only $\frac{1}{18}$ of its weight; at 16°, according to Thomson, $\frac{1}{11}$ of its weight, or 33 times its volume, the specific gravity of the solution being 1·0513; according to Davy, 30 times —according to Dalton, 20 times—according to Saussure, 44 times its volume, at 18°. According to Berthollet, the specific gravity of water saturated with sulphurous acid is 1·040. The combination of the gas with water is attended with a slight development of heat. Ice introduced into the gas quickly melts.

The liquid is colourless, has the odour of burning sulphur, and an acid, drying taste. When the water in the solution freezes—which effect takes place a few degrees below 0°—the gas does not escape; and only a portion is evolved on boiling, unless the boiling be continued for a very long time. When the solution is exposed to the air, part of the gas escapes, the rest remaining in the form of sulphuric acid. The aqueous acid gives with hydrosulphuric acid, after a while, a milk-white cloud, and with selenious acid, a red cloud. It decolorizes sulphate of manganic oxide, and hypermanganate of potassa, and precipitates metallic gold from the chloride. The smallest quantity of sulphurous acid evolves sulphuretted hydrogen when treated with zinc and hydrochloric acid* (Fordos & Gélis,)—and gives a blue colour to paper moistened with starch and iodic acid. (Orfila.)

b. The *Sulphites*, or salts produced by the combination of sulphurous acid with salifiable bases are obtained by passing sulphurous acid gas into water in which the bases, either pure or in the state of carbonates, are dissolved or diffused. They are inodorous, and when soluble, have a sharp, brisk flavour. Monosulphite of potassa or soda has an alkaline reaction, while the corresponding bi-salts are neutral. The sulphites of the fixed alkalis, sulphite of lead, and the sulphites of some of the other heavy metallic oxides are resolved by ignition into $\frac{3}{4}$ sulphate and $\frac{1}{4}$ sulphide: *e. g.*

$$4\,(PO, SO^2) = 3PbO, SO^3 + PbS.$$

Other sulphites, those of the earths for instance, give off their acid, while the base remains behind. Most of the heavy metallic sulphites, when heated with charcoal, hydrogen, potassium, sodium, iron, zinc, tin, manganese, or antimony, are reduced to the state of sulphides, the bodies just mentioned abstracting oxygen from both the acid and the metallic oxide. The alkaline sulphites in the state of solution in water are converted by digestion with sulphur into hyposulphites and trithionates: small quantities of hydrosulphuric acid or of an alkaline sulphide likewise convert

* Protochloride of tin is recommended by Wackenroder as the best reagent for detecting traces of sulphurous acid. The solution to be tested is to be acidulated with hydrochloric acid—mixed with solution of protochloride of tin—and the containing vessel covered with a glass plate, to the under surface of which is attached a piece of paper moistened with solution of acetate of lead. If sulphurous acid be present, or any of the other acids of sulphur which evolve it on being mixed with hydrochloric acid—sulphuretted hydrogen will be given off, and will blacken the paper. (*Pharmac. Centralblatt.* 1846, p. 615.) [W.]

them, without precipitation of sulphur into hyposulphites;—with larger quantities of the same reagents, the conversion is accompanied by precipitation of sulphur (II., 160). By exposure to the air, especially in the moist state—also by contact with nitric oxide gas, excess of heated nitric acid, or with chlorine water, solution of hypochlorous acid or its salts, or with nitre and certain heavy metallic oxides in a state of fusion—the sulphites take up an additional dose of oxygen, and are converted into sulphates, their neutrality remaining unaltered. In a similar manner, the alkaline sulphites decolorize manganate of potassa mixed with sulphuric acid, and likewise the salts of sesqui-oxide of iron, which are first reddened by them and then converted into salts of protoxide of iron. The alkaline sulphites likewise precipitate selenium, in the form of a red powder, from selenious acid mixed with hydrochloric acid,—and tellurium, as a black powder, from solution of chloride of tellurium;—throw down light-brown sulphite of suboxide of copper from salts of protoxide of copper, on boiling,—and metallic gold from chloride of gold, on the addition of hydrochloric acid. With nitrate of silver, they give a precipitate which is white at first, but changes slowly in the cold, and quickly on boiling, into a brilliant specular coating of metallic silver. From protochloride of tin dissolved in hydrochloric acid, the smallest quantity of an alkaline sulphite gradually throws down a brown precipitate of protosulphide of tin.

The sulphites are not decomposed by carbonic or boracic acid; but they are decomposed by phosphorous, sulphuric, hydrochloric, arsenic acid, &c., without precipitation of sulphur: if there is not much water present, the sulphurous acid escapes with effervescence.

Among the simple sulphites, only the ammonia, potassa, soda, and lithia salts are soluble in water. Hence a solution of either of these salts gives with the earthy alkalis, earths, and heavy metallic oxides, precipitates which are soluble in dilute hydrochloric or nitric acid. If however the precipitate of sulphite of baryta or sulphite of lead is boiled with nitric acid, an insoluble precipitate of the corresponding sulphate is formed. The acid sulphites are all soluble in water.

¶ Dr. Muspratt has made an elaborate investigation of the salts of sulphurous acid (*Ann. Pharm.* 50, 259)—by which he has shown that a great number of these salts are precisely analogous in composition to the corresponding carbonates, and are moreover isomorphous with them. The following table exhibits this analogy of composition in the two classes of salts, in those cases in which it has been observed:

Sulphites.	*Carbonates.*
$KO, SO^2 + 2HO$	$KO, CO^2 + 2HO$
$KO, SO^2 + HO, SO^2$	$KO, CO^2 + HO, CO^2$
$NaO, SO^2 + 10HO$	$NaO, CO^2 + 10HO$
$NaO, SO^2 + HO, SO^2$	$NaO, CO^2 + HO, CO^2$
$NaO, SO^2 + HO, SO^2, + 8HO$	$NaO, CO^2 + HO, CO^2 + 8HO$
BaO, SO^2	BaO, CO^2
SrO, SO^2	SrO, CO^2
$MgO, SO^2 + 3HO$	$MgO, CO^2 + 3HO$
$MnO, SO^2 + 2HO$	$MnO, CO^2 + 2HO$
PbO, SO^2	PbO, CO^2
AgO, SO^2	AgO, CO^2.

Many of the sulphites which are insoluble in water are soluble in aqueous solution of sulphurous acid; *e. g.* the sulphites of baryta, strontia, and lime, another property in which these salts resemble the carbonates.¶

c. Sulphurous acid gas is absorbed by alcohol and other organic liquids.

F. Hyposulphuric Acid. S^2O^5.

Unterschwefelsäure, Acide hyposulfurique, Acidum hyposulphuricum.

[illegible] This acid is produced on bringing aqueous sulphurous acid [illegible] in contact with peroxide of manganese (not with brown peroxide of [illegible] Gay-Lussac. (Scheme 106.)

$MnO^2 + 2SO^2 = MnO, S^2O^5$.

[illegible] peroxide of manganese is diffused through 5 parts of water, [illegible] gas passed through the liquid, the temperature rises [illegible] and hydrated manganic oxide (Mn^2O^3, HO) separates in [illegible] Sulphate of manganese is always produced [illegible] hyposulphate. ($MnO^2 + SO^2 = MnO, SO^3$.) [illegible] the hyposulphuric acid thus formed varies from 137 to 370 parts, [illegible] parts of hyposulphuric acid produced; it appears to be [illegible] temperature of the liquid is higher, and the manganese [illegible] The presence of hydrated manganic oxide in the [illegible] gives rise to the production of sulphate and likewise of [illegible]

$Mn^2O^3 + 2SO^2 = MnO, SO^3 + MnO, SO^2$;

[illegible] of solution. Hyper-manganic acid [illegible] by contact with aqueous [illegible] of manganous oxide by contact with aqueous [illegible] liquid sulphurous acid has no action on [illegible]

[illegible] does not appear to be formed when sulphurous [illegible] oil of vitriol strongly cooled. In this case, [illegible] a frozen mass is produced, which, on [illegible] If oil of vitriol be agitated in the [illegible] acid gas. If oil of vitriol [illegible] a small quantity of the [illegible] sulphurous acid, only a [illegible] specific gravity, and [illegible] of vitriol, diminishing its specific gravity, and [illegible] but without making it fume; [illegible] of sulphurous acid rises to the top of the oil of [illegible] the sulphurous acid [illegible] distinct layer above it. (Bussy.) A peculiar compound [illegible] acid with anhydrous sulphuric acid will be described [illegible]

[illegible] Acid.

[illegible] is not known to exist in the separate state.

Calculation.			Or:		
[illegible]	32	44.44	SO^2	32	44·44
[illegible]	40	55·56	SO^3	40	55·56
[illegible]	72	100·00	S^2O^5	72	100·00

$S^2O^5 = 2 . 201·17 + 5 . 100 = 902·34$. (Berzelius.)

[illegible] a. With Water. [illegible] of *Hyposulphuric Acid*. Sulphurous acid gas is passed [illegible] in which powdered manganese is suspended. Sulphate [illegible] of manganous oxide are then produced; the manganous [illegible] sulphuric acid are precipitated by excess of baryta water— [illegible] filtered—and the excess of baryta separated by passing [illegible] gas through the liquid, and subsequent boiling. The [illegible] of baryta is next to be purified by evaporation and crys- [illegible]

tallisation—the crystals dissolved in water—the baryta precipitated by sulphuric acid cautiously added in the exact proportion required—and lastly, the filtrate concentrated, first by warming, and afterwards by evaporation in vacuo over sulphuric acid, till it attains a specific gravity of 1·347. (Gay-Lussac.) Heeren uses 1 part of very finely pounded manganese to 5 parts of water—precipitates the filtrate, not by baryta water, but by solution of hydrosulphate of baryta—decomposes the excess of this reagent by agitating the liquid with carbonic acid gas—filters—boils the solution in order to drive off the sulphuretted hydrogen and carbonic acid, and precipitates the carbonate of baryta—then filters the liquid, and evaporates to the crystallizing point, &c. &c.

The hydrate of hyposulphuric acid is a transparent and colourless liquid, inodorous, and of strongly acid taste. By further evaporation in vacuo, or by being heated to 100°, it is decomposed into sulphurous acid, which escapes, and sulphuric acid, which remains behind. (Gay-Lussac.) When exposed to the air, it is slowly converted into sulphuric acid. It is not oxidated in the cold by strong nitric acid, chlorine water, or sulphate of manganic oxide (Gay-Lussac); nor yet by aqueous hypochlorous acid. (Balard.) It does not take oxygen from aqueous hypermanganic acid, peroxide of lead, or the oxides of mercury, silver, gold, and platinum, dissolved in acids; neither does it decompose hydrosulphuric or hydriodic acid dissolved in water. (Heeren.) When dilute, it dissolves zinc (and iron, according to Heeren), with evolution of hydrogen, but without decomposition of the acid itself. (Gay-Lussac.)

β. The acid is miscible with larger quantities of water.

b. The salts produced by the union of this acid with salifiable bases are called *Hyposulphates:* in the normal state they contain 2 atoms of sulphur and 5 atoms of oxygen for every atom of base. When heated—sometimes even at 100°—they evolve 1 atom of sulphurous acid and leave 1 atom of neutral sulphate. In the state of aqueous solution, they are not oxidized at ordinary temperatures, either by exposure to the air, or by nitric acid, chlorine, hypochlorous acid, hypermanganic acid, peroxide of lead, or by the oxides of mercury, silver, gold, and platinum dissolved in acids. But at a boiling heat, they are oxidized by nitric acid or chlorine, 2 atoms of sulphuric acid being produced for each atom of base. In the solid state, they are decomposed by oil of vitriol, even at ordinary temperatures, sulphurous acid escaping with violent effervescence. But in the state of aqueous solution, they are not decomposed by sulphuric or hydrochloric acid till the liquid is boiled, and then they are resolved into sulphurous acid and a sulphate, without deposition of sulphur. In consequence of this evolution of sulphurous acid, a solution of a hyposulphate boiled for a few minutes with either of the acids just mentioned, decolorizes hypermanganic acid, precipitates sulphur from hydrosulphuric acid, and gold from the chloride of that metal. All hyposulphates are soluble in water. (Gay-Lussac; Heeren; H. Rose.)

G. Sulphuric Acid. SO^3.

Vitriolic acid, Perfect Sulphuric acid, Schwefelsäure, Acide Sulfurique, Acidum sulphuricum, Acidum vitriolicum.

This acid probably exists combined with water in certain volcanic springs: it is also found in large quantities, both in the organic and inorganic kingdoms, in combination with ammonia, potassa, soda, baryta, strontia, lime, magnesia, alumina, the protoxide and sesqui-oxide of ura-

nium, the oxides of cobalt, zinc, and lead, the protoxide and sesqui-oxide of iron, and the protoxide of copper.

Formation. 1. From Sulphur. *a.* In well-washed flowers of sulphur exposed to the air for several weeks, a certain quantity of sulphuric acid is gradually formed. (John, *Schw.* 14, 417; Wagenmann, *Pogg.* 24, 601.) Milk of sulphur kept in a dry state for 18 years was found by Wackenroder to be free from sulphuric acid. (*N. Br. Arch.* 26, 180.) *b.* By the action of chlorine water, hypochlorous acid and its salts, by nitric acid, aqua regia, by a mixture of nitric acid and chlorate of potassa, and, at a red heat, by alkaline iodates, hyperiodates, bromates, chlorates, perchlorates, nitrites and nitrates.—2. From pentathionic, tetrathionic, and trithionic acid, by elevation of temperature, or by the action of chlorine on nitric acid.—3. From sulphurous acid. *a.* A dry mixture of two measures of sulphurous acid gas and one measure of oxygen remains unaltered: but, if water be present, a very gradual condensation takes place, and sulphuric acid is produced;—in contact with red-hot platinum, especially if water be present, the effect takes place very quickly. (Per. Phillips, *Pogg.* 24, 610.) If the undried mixture of sulphurous acid and oxygen or atmospheric air be passed through a tube kept at a low red heat, and containing spongy platinum or platinum wire, nearly all the sulphurous acid is converted into oil of vitriol. (Phillips; Magnus.) If the tube contains pieces of glass instead of platinum, the quantity of sulphuric produced is small; and if it be empty, still less. (Magnus, *Pogg.* 24, 610.) Platinum-black dried in the air converts the mixture of sulphurous acid and oxygen into fuming oil of vitriol. (Döbereiner, *Pogg.* 24, 609.)—*b.* When sulphurous acid gas is mixed with oxygen (or air), nitric oxide, and vapour of water, the nitric oxide first takes up oxygen and is converted into hyponitric acid, and then gives it up to the sulphurous acid, which is thereby converted into sulphuric acid. (For a more exact explanation of this reaction, on which the preparation of common oil of vitriol depends, see *Nitrogen and Sulphur.*)—*c.* By chlorine-water, hypochlorous acid and its salts, nitric acid, peroxide of hydrogen, and the peroxides of certain metals. In the last-mentioned case, the sulphuric acid formed by the oxidation combines with the salifiable base produced by the reduction of the peroxide.—4. From hyposulphuric acid. *a.* By simply heating the acid. *b.* By heating it together with nitric acid.—5. From hydrosulphuric acid, and from metallic sulphides, hyposulphites, pentathionates, tetrathionates, trithionates, sulphites, and hyposulphates. (*q. v.*)

Preparation of Anhydrous Sulphuric acid.—Fuming oil of vitriol is heated in a retort, the neck of which passes air-tight into a perfectly dry receiver surrounded with ice. No luting or paper must be used in making the connexion. Anhydrous sulphuric acid distils over first, and is followed by hydrated acid: hence the receiver must be changed after a while. Anhydrous sulphate of antimony or of bismuth may likewise be used. (Graham, *Lehrb.* 2, 140.) By mixing three parts of dry sulphate of soda with two parts of oil of vitriol, heating the mixture to commencing redness, and till it ceases to boil—pounding it up quickly after cooling—and igniting it in a porcelain retort, a nearly anhydrous acid is obtained in brittle tubular masses. (Berzelius.)

¶ According to the experiments of Barreswil (*Compt. Rend.* 25, 30), anhydrous sulphuric acid may be obtained by distilling common oil of vitriol with anhydrous phosphoric acid. ¶

Properties. Slender needles arranged in feathery and star-shaped groups and forming a white, opaque, asbestos-like mass. Tough and difficult to cut. (F. C. Vogel.) Sp. gr. at 13° = 1·9546 (Morveau), and in the liquid state at 20° = 1·97. (Bussy.) Fuses between 12° and 19° (F. C. Vogel), between 22° and 24° (Fischer), at 25°, or a little below (Bussy),—forming a liquid which, according to Bussy, is thinner than common oil of vitriol, and probably colourless when pure, but generally has a brown colour, possibly arising from a small quantity of organic matter introduced in the form of dust and decomposed by the acid. According to Wach, the acid when dried to the utmost possible extent, assumes at 62·5° the appearance of moistened cotton, and melts at 100° to a colourless liquid. It boils between 52° and 56°. (Fischer, *Pogg.* 16, 119.) [These two statements contradict each other.] The vapour is colourless; its specific gravity has already been given (I., 279). Exposed to the air at ordinary temperatures, the acid forms thick, white, suffocating fumes. It may be held for a while between the dry fingers, but soon produces a penetrating sensation. (F. C. Vogel.) Hisses violently when thrown into water. Produces dense white fumes in the air. Chars wood, paper, and many other organic bodies very rapidly. Very corrosive and poisonous; its solution in water has a strongly acid taste, and reddens litmus, whereas the anhydrous acid does not redden dry litmus paper. With a solution of chloride of barium it gives a precipitate insoluble in hydrochloric acid. The following reactions reach their limits when one part of anhydrous sulphuric acid is diluted with the following quantities of water: Reddening of litmus paper, immediate, 25,000; in an hour, 62,500; precipitation of chloride of barium, 75,000; of chloride of calcium, 310; of acetate of lead, 5,000 parts of water. (Harting, *J. pr. Chem.* 22, 47.)

	Calculation.		Berzelius.	Richter.	Klaproth.	Bucholz.	Berthollet.
S	16	40	40·14	42·05	42·3	42·5	43·762
3O	24	60	59·86	57·95	57·7	57·5	56·238
SO^3	40	100	100·00	100·00	100·0	100·0	100·000

	Vol.	Sp. gr.	Vol.	Sp. gr.		Vol.	Sp. gr.
Sulphur vapour	1	6·6556 =	$\frac{1}{6}$	1·1093	Sulphurous acid gas	1	2·2186
Oxygen gas	9	9·9837 =	$1\frac{1}{2}$	1·6639	Oxygen gas	$\frac{1}{2}$	0·5546
Sulphuric acid vap.	6	16·6393 =	1	2·7732	Sulphuric acid vap.	1	2·7732

(SO^3 = 201·17 + 3 . 100 = 501·17. Berzelius.)

Decompositions. The acid when passed through a red-hot porcelain tube is resolved into a mixture of two volumes of sulphurous acid gas and one volume of oxygen. (Berzelius.)—2. Phosphorus after a while takes fire in the vapour of anhydrous sulphuric acid at ordinary temperatures, and deposits sulphur in the form of a thick crust. (F. C. Vogel.)—3. Phosphuretted hydrogen gas passed over the anhydrous acid at ordinary temperatures produces a copious evolution of sulphurous acid, and deposits phosphoric oxide. (H. Rose, *Pogg.* 24, 140.) It generates yellow fumes, which condense in the form of a yellow powder; and on the following day a blue liquid (sulphur dissolved in anhydrous sulphuric acid) is found to have been formed. (Aimé, *J. Pharm.* 20, 87, also *J. pr. Chem.* 6, 79.)—4. Mercury when heated acts rapidly on the acid, abstracting one atom of its oxygen, and forming sulphate of mercuric oxide, with evolution of sulphurous acid. (*Scheme* 23.) *F. C. Vogel.* At ordinary temperatures, the vapour of the anhydrous acid does not act upon zinc,

tin, lead, iron, copper, mercury, or silver. (Bizio, *Giorn. di Fis.* 8, 407; also *Quart. J. of Sc.* 21, 176.) ¶ At a red heat, however, iron decomposes the vapour of anhydrous sulphuric acid, producing a fused, blistered mass having a greyish metallic aspect, and consisting of monosulphide of iron and magnetic oxide:

$$4SO^3 + 13 Fe = 3 (Fe^3 O^4) + 4FeS.$$

Zinc, under similar circumstances, is converted into a mixture of oxide and sulphide:

$$SO^3 + 4Zn = 3ZnO + ZnS.$$

(Albert d'Heureuse, *Pogg.* 75, 255.) ¶

Compounds of Anhydrous Sulphuric acid with Sulphur. F. C. Vogel has discovered that anhydrous sulphuric acid combines with sulphur in several proportions, forming a brown, a green, and a beautiful blue compound, the first of which contains the largest, and the last the smallest quantity of sulphur. The green compound is solid at ordinary temperatures; the other two are liquid. When heated they evolve sulphurous acid and sometimes a small quantity of anhydrous sulphuric acid, while oil of vitriol remains behind (a proof that water was previously contained in the compound)—associated with sulphur, in the case of the green compound, but without sulphur in that of the blue. In contact with water, they are resolved, with great development of heat, into sulphuric acid, sulphurous acid, and sulphur. In the blue compound, phosphorus takes fire instantly, producing a deposition of sulphur. The blue compound forms sulphates with the alkalis and earths, the combination being attended with evolution of sulphurous acid gas.

Wach prepared these compounds by placing washed and well-dried flowers of sulphur and anhydrous sulphuric acid, in alternate layers in a bent glass tube, which was afterwards sealed, and leaving them to act upon each other at a temperature between 16° and 19° (60°—66° F.). The sulphur was first converted, with slight rise of temperature and evolution of gas, into a thick red-brown liquid, which subsequently, by taking up more acid, assumed a brown, green, or blue colour.

Brown Compound. Produced by the action of 8 pts. (1 At.) of sulphur on 10 pts. (2 At.) of sulphuric acid. (When from 9 to 10 parts of sulphur are used with 40 parts of acid, a portion of sulphur remains undissolved.) Clear, brown liquid, not solidifying even at the greatest degree of cold that could be produced. When exposed to daylight at ordinary temperatures, it deposits needles of sulphur in the course of 24 hours. Begins to boil in the sealed tube at 37·5 (99·5 F.), and separates into a brownish-yellow and a brown stratum, the latter being at the bottom. Sulphur is then deposited, and liquid sulphurous acid, containing at most 0·4 per cent. of anhydrous sulphuric acid, collects in the cold arm of the tube. This, when poured back into the heated arm, does not mix with the other liquid on agitation, but forms a colourless stratum on the top of it.

Green Compound. Formed by the combination of 6 pts. sulphur and 40 pts. anhydrous acid. (With 5 pts. sulphur, a liquid is formed which is blue by reflected, and greenish blue by transmitted light.) This compound is of a deep green colour, and perfectly liquid, even in the cold (contrary to Vogel's assertion). Exposed to daylight at ordinary temperatures, it soon turns brown and deposits sulphur in flakes. Turns brown almost instantly when heated.

Blue Compound. Formed by the union of 4 pts. (1 At.) sulphur and 40 pts. (4 At.) sulphuric acid. (1 to 3 parts sulphur and 40 of acid produce a mixture of the blue compound with unaltered acid.) Indigo-blue, transparent liquid, not freezing at—22·5 (—8·5°F.). By exposure to daylight it gradually becomes of a paler blue colour; and in 6 weeks, of a brownish-yellow, a few flakes of sulphur also separating from it: in direct sunshine, this change takes place in 8 hours. If the arm of the tube containing the compound be cautiously heated to 56° (133° F.) while the other arm is cooled to — 10° (+ 14° F.) it separates into a lower stratum of a brownish colour, and an upper stratum of a wine-yellow tint, and begins to boil—the ebullition then continuing quietly even at 31° (88° F.), with precipitation of pale-yellow sulphur, till the upper stratum of liquid has entirely disappeared, and passed over to the cold arm of the tube in the form of liquid sulphurous acid. This liquid contains about 5 per cent. of sulphuric acid. When poured back upon the brown residue in the other arm, it does not mix with that liquid but forms a colourless stratum on the top of it. The brown residue, which does not boil even at the melting point of sulphur, presents the characters of oil of vitriol [consequently, water could not have been completely excluded]. The transparent and therefore partially hydrated acid likewise forms the blue compound with sulphur. [Thus far Wach.]

When the vapour of anhydrous sulphuric acid is passed into a tube containing sulphur—moisture being as far as possible excluded—and the tube sealed, the blue compound is formed at particular places only, and is immediately decomposed again, with formation of a thinly fluid compound of anhydrous sulphurous and sulphuric acid. But if a trace of moisture be present, the sulphur forms—with slight evolution of gas—a liquid which is first brown, then green, and lastly blue. This becomes paler, and is converted, in the course of a day or two, into a colourless mixture of the two acids. On opening the tube, the sulphurous acid escapes with violence, and the rest of the sulphur often turns blue again by combining with the remaining sulphuric acid. Oil of vitriol dissolves sulphur in very small quantity only, and very slowly. (Fischer, *Pogg.* 16, 119.

When ammoniacal gas is passed over the blue liquid, violent action takes place, the liquid assumes a carmine colour, and is ultimately converted into a white mass of ammoniacal salts with reddish spots here and there. Water dissolves these salts, and leaves sulphur behind. (H. Rose, *Pogg.* 32, 98.)

Compound of Anhydrous Sulphuric acid with Sulphurous acid. In order that sulphurous acid may be abundantly absorbed by sulphuric acid, both acids must be as nearly anhydrous as possible. The sulphurous acid gas is passed through a tube four feet long filled with freshly ignited chloride of calcium, into a bottle closed with a cork and cooled to zero, containing the anhydrous sulphuric acid. The liquid compound as it forms is poured off from time to time from the remaining sulphuric acid. This compound is a thin liquid (brownish from the action of the sulphuric acid on the cork), which evaporates rapidly in the air, forming an exceedingly thick cloud, with the odour of sulphurous acid, and sometimes leaving only a trace of oil of vitriol. It contains from 67·68 to 72·9 per cent. of sulphurous acid; which nearly agrees with the formula, $SO^2 + 2SO^3$.—When kept for a long time it loses part of its sulphurous acid.—With water it effervesces violently, evolving sulphurous acid. It absorbs dry ammoniacal gas, forming a yellowish body, which

behaves like a mixture of anhydrous sulphate of ammon, and anhydrous sulphite of ammon. (H. Rose, *Pogg.* 39, 173.)

Other Compounds of Sulphuric acid. *a.* With Water. Sulphuric acid has a peculiarly strong affinity for water: its combination with the first atom of that substance is attended with great development of heat. When 4 parts of anhydrous sulphuric acid are mixed with 1 part of water, the resulting compound is converted into vapour, with explosion and emission of light. (F. C. Vogel.) The acid when exposed to the air, produces white fumes, because its vapour combines with the aqueous vapour in the air, and forms oil of vitriol.

α. In the distillation of fuming oil of vitriol (*Vid.* p. 176), a compound of a very large quantity of sulphuric acid with a very small quantity of water, passes over after the anhydrous acid, and solidifies in large transparent tabular crystals.

β. Nordhausen, German, Fuming, Brown Oil of Vitriol. This liquid is prepared by long continued ignition of green vitriol previously freed from its water of crystallization, and converted into sulphate of ferric oxide by heating it in the air: the material is placed in earthen retorts heated in a reverberatory furnace. The earthen receivers are kept cool, and if the calcined green vitriol is quite dry, a little water, or common oil of vitriol, according to more recent practice, is put into them; otherwise the vapours of anhydrous sulphuric acid which pass over would not be properly condensed. The same liquid may likewise be formed by mixing anhydrous sulphuric acid with common oil of vitriol. *Properties.* Light brown (in consequence of a little organic matter), viscid like oil; of specific gravity 1·896, according to Thomson; of 66°—68° B. according to Bussy. Solidifies a little above 0°, diminishing in bulk, and forming colourless, transparent crystals. Fumes in the air; boils between 40° and 50° (Bussy), and is thereby resolved into anhydrous acid, which passes off in vapour, and sometimes amounts to 25 per cent., and common oil of vitriol which remains behind. (The boiling point rises as the quantity of anhydrous acid diminishes.) By mixing it with a small quantity of water, whereby great heat is evolved, it is converted into common oil of vitriol. It must therefore be regarded as a compound of one atom of water with several atoms of anhydrous sulphuric acid, or of ordinary oil of vitriol with anhydrous acid. It is often contaminated with sulphurous acid, selenium, earthy matters, oxide of iron, and organic matter. When common English oil of vitriol has been put into the receivers, it contains the same impurities as that liquid itself.

γ. Sulphuric acid with one atom of Water. Common Oil of Vitriol, Concentrated Sulphuric acid. This is the most intimate compound of sulphuric acid and water. It is left behind when fuming oil of vitriol is heated till all excess of acid is driven off, and likewise when dilute sulphuric acid is boiled till the residue no longer increases in density.

It is prepared on the large scale, as *English* or *White Oil of Vitriol*, by burning sulphur mixed with $\frac{1}{8}$ of its weight of nitre in a spacious chamber, called the *Leaden Chamber*, constructed principally of lead plates, filled with air and aqueous vapour, and having its floor covered with water. Sometimes also the sulphur is burned by itself, vessels containing nitric acid being placed in the leaden chamber, or vapours of nitric or hyponitric acid being passed into it. The nitrous gas evolved from the nitre or nitric acid takes oxygen from the air, and transfers a portion

of it to the sulphurous acid produced by the combustion of the sulphur. (*Vid.* p. 176, also *Nitrogen and Sulphur.*) The water impregnated with sulphuric acid (*Sauerwasser*), which has a specific gravity of about 1·2 or 1·3, is first concentrated in leaden vessels to the density of at most 1·78, and afterwards distilled in vessels of glass or platinum, till the less intimately combined water, together with the nitric and hydrochloric acids, has passed off, and the oil of vitriol begins to evaporate in white fumes. In general, however, the distillation is not carried quite so far, so that common English oil of vitriol is really a mixture of HO,SO^3 and $2HO,SO^3$. Iron pyrites or copper pyrites is sometimes burnt instead of sulphur;—or sulphate of lime is ignited with charcoal; the sulphide of calcium thereby produced diffused through water; carbonic acid gas, generated by the following ignition of sulphate of lime, passed through the liquid; and the sulphuretted hydrogen thereby evolved from the sulphide of calcium burnt in the leaden chamber. (Thaulow, *N. Br. Arch.* 26, 165.) Instead of inducing the transfer of atmospheric oxygen to the sulphurous acid through the medium of nitric oxide, the sulphurous acid generated by the combustion of the sulphur may be passed, mixed with air, through a strongly ignited porcelain or platinum tube filled with platinum wire or spongy platinum (p. 176; Per. Phillips, *Pogg.* 24, 610). On the small scale, the aspirator may be used for this purpose. (Brunner.)

Common oil of vitriol may contain the following impurities: Excess of water (by which it is rendered specifically lighter, and crystallizable by a moderate degree of cold); hydrochloric acid (from impurities in the nitre); nitric oxide, nitrous and nitric acids; potassa (from the nitre, first observed by Göttling, *Taschenb.* 1782, 119); oxide of lead (derived from the leaden vessels,—separates on diluting with water, as a white precipitate of sulphate of lead); and lastly, from accidental impurities in the sulphur or pyrites consumed; selenium; lime; magnesia; titanium (Pfaff, *Schw.* 18, 283); arsenic; oxide of zinc; and binoxide of tin (Berzelius, *Schw.* 23, 313; *Pogg.* 33, 24); sesqui-oxide of iron (forming a white deposit of ferric sulphate, which disappears on diluting the acid with water); oxide of copper (Berzelius and Trommsdorff, *N. Tr.* 3, 2, 64 and 4, 1, 130); and mercury (Berzelius, *Schw.* 23, 313). Many of these substances are not dissolved by the oil of vitriol, but merely form a sediment in it. (*Vid.* Giese, *Scher. Ann.* 6, 1.) Organic matter accidentally introduced into oil of vitriol imparts to it a brown colour which disappears on boiling.

Hydrochloric acid. Mullen (*Quart. J. of Sc.* 22, 231 and *N. Quart. J. of Sc.* 2, 258) and Johnston (*M. Quart. J. of Sc.* 3, 154) found that peroxide of manganese or red lead, free from chlorine, evolved chlorine gas when treated with sulphuric acid. Kane (*N. Quart. J. of Sc.* 4, 286) pointed out that oil of vitriol contains from 0·03 to 0·14 per cent. of hydrochloric acid, whence the preceding observation is easily explained. (See the supposed formation of peroxide of hydrogen by the mutual action of sulphuric acid and metallic peroxides, p. 74.)

The presence of *nitric oxide, nitrous acid,* or *nitric acid* in oil of vitriol, is best detected by the addition of a solution of sulphate of ferrous oxide, which produces a purple colour, even if the nitrogen-compound amount to no more than $\frac{1}{10,000}$ of the whole. (Desbassins, *J. Chim. Med.* 11, 508.) A tolerably strong solution of the ferrous sulphate is to be cautiously poured upon the surface of the oil of vitriol, so as to form a layer one-fourth as deep as the oil of vitriol itself. The red colour appears at the common surface of the two liquids: if it should disappear after a time, it may be restored by agitation. (Wackenroder, *Ann. Pharm.* 18, 152.) An-

other mode of making the experiment is to pour carefully half a gramme of water on the surface of 50 grammes of oil of vitriol—wait till the heat thereby developed, which would destroy the colour, has been dissipated—and then add 10 drops of the iron solution, mixing slowly, so that the liquid may not become heated. In this manner, 1 part of nitric acid, nitrous acid, or a nitrate, mixed with 1429 parts of oil of vitriol, may be made to give a bright red; with 142,900, a pale red; and with 333,333, a pale rose-colour; while with 500,000 parts of oil of vitriol (the limit) the colouring is just perceptible. (Jacquelain, *Compt. Rend.* 14, 643.)

Every sample of English oil of vitriol examined by E. Baruel (*J. Chim. Med.* 12, 180; also *Ann. Pharm.* 22, 286) exhibited the reaction just described, but in very different degrees. Oil of vitriol thus contaminated dissolves platinum at a boiling heat; yields, when distilled with common salt, hydrochloric acid mixed with free chlorine; and forms with indigo, not a pure blue, but a greenish blue solution. (E. Baruel.)—The nitrogen compound present is nitrous acid; for nitric acid mixed with oil of vitriol passes off at the beginning when the liquid is distilled, whereas the azotised compound actually present in the oil of vitriol is intimately combined with it. Oil of vitriol of this description likewise decolorizes sulphate of manganic oxide, instantly precipitates sulphur from hydrosulphuric acid water, and when diluted with 2 parts of water, evolves the odour of nitrous acid. (Wackenroder, *Ann. Pharm.* 18, 152.)—The azotised compound usually occurring in common oil of vitriol is not nitric or nitrous acid, but nitric oxide. When oil of vitriol of this kind is distilled, the first $\frac{1}{4}$ of the liquid pass over free from nitric oxide, and consequently do not redden a solution of green vitriol. The following portions of the distillate contain more and more nitric oxide; and the residue is so rich in that compound, that when diluted with water, it evolves nitric oxide gas in abundance, and if contact of air be prevented, the gas so evolved is colourless. If oil of vitriol containing nitric oxide be diluted with water till its density is reduced to 1·2, it gives up all its nitric oxide when concentrated to the strength of oil of vitriol. From this it would appear that the dilute acid of the leaden chambers must give up all its nitric oxide during the process of concentration; but on the one hand, it is admitted continuously into the platinum retorts which already contain a more concentrated acid; and on the other hand, nitric acid is often mixed with the oil of vitriol at a subsequent stage of the process, in order to destroy the organic matter which colours it brown. (A. Rose, *Pogg.* 50, 161.)

Nitric acid in oil of vitriol may be distinguished from nitrous acid and nitric oxide by the following characters: If oil of vitriol which contains it be mixed with water and hydrochloric acid, it will dissolve gold leaf on boiling; when diluted with water and boiled with solution of indigo, it destroys the colour. (Jacquelain.) When it is subjected to distillation, the nitric acid passes over with the first portions; afterwards pure oil of vitriol is obtained, and finally an acid which may contain nitrous acid (or nitric oxide) in solution. (Wackenroder; A. Rose.)

To purify oil of vitriol from the oxides of nitrogen, E. Baruel heats 21 parts of it with 1 part of sulphur, at a temperature between 150° and 200° for several hours, till the liquid, which gradually acquires a brown colour, evolves the odour of sulphurous acid. To expel the sulphurous acid thus produced, Jacquelain mixes the oil of vitriol with chlorine water, and boils for a few minutes till the hydrochloric acid is driven off. Wackenroder heats the oil of vitriol with paper, or better, with sugar, till the liquid, which at first turns black, begins to boil and again becomes

colourless: the addition of a little fuming oil of vitriol hastens the decolorization. Pelouze (*Ann. Chim. Phys.* 77, 52) heats the oil of vitriol to 160° (320° F.), with from $\frac{1}{10}$ to $\frac{1}{2}$ per cent. of sulphate of ammonia (the quantity being determined by previous trials); the ammonia and nitric oxide or nitric acid are then resolved into water and nitrogen gas. The ammoniacal salt may be added immediately to the dilute acid which is to be evaporated in the leaden pans; and thus the corrosion of the platinum retort will be avoided. A. Rose heats the oil of vitriol diluted with twice its weight of water in a retort till sulphuric acid begins to distil over.

Arsenic, which has been often detected—and frequently in considerable quantity—in oil of vitriol, by Martius, (*Schw.* 3, 363), Wackenroder (*Repert.* 47, 337), A. Vogel (*J. pr. Chem.* 4, 232), Dulk (*Berl. Jahrb.* 34, 1, 247), Ficinus (*Ann. Pharm.* 15, 78), and Arthaud (*J. Chim. Med.* 16, 620), appears to exist in it, for the most part, in the state of arsenious acid. Very small quantities of it may be detected by diluting the oil of vitriol with water, supersaturating with carbonate of potassa, filtering from the precipitated sulphate of potassa, washing with a small quantity of water, evaporating, supersaturating with hydrochloric acid, and passing hydrosulphuric acid gas through the liquid. (Dulk.) Arsenical oil of vitriol diluted with water, gives with hydrosulphuric acid, a precipitate of sulphide of arsenic and sulphide of lead, often amounting to more than one per cent., and deposits after a while, a little more sulphide of arsenic: the greater part of the arsenic appears therefore to exist in the form of arsenious acid, but a small quantity likewise in the form of arsenic acid. This supposition is corroborated by the reddish tint ultimately assumed by the precipitate, which the arsenical oil of vitriol neutralized with ammonia gives with nitrate of silver. (Wackenroder.) A. Vogel found nothing but arsenious acid. According to his observations, three-fourths of the oil of vitriol may be distilled over free from arsenic. According to Wackenroder, the distillate contains arsenic, and therefore the oil of vitriol—in order to purify it from arsenic and lead—must be diluted with water, saturated with hydrosulphuric acid, left to stand for several days in a close vessel, decanted from the precipitated sulphides, and exposed to the air, that the excess of hydrosulphuric acid may escape. According to Ficinus, also, arsenic passes over with the distillate; he therefore recommends that hydrated ferric oxide be added to the oil of vitriol, and the distillation stopped when two-thirds of the liquid have passed over. The residue in the retort poured off from the white sediment, is likewise free from arsenic.

When oil of vitriol is evaporated in a platinum dish, the less volatile impurities remain behind.

Rectified, Distilled, or *Purified Oil of Vitriol* is obtained by distilling either the fuming or the English oil of vitriol in glass retorts or platinum stills. Fuming oil of vitriol is the best for this purpose; for after the anhydrous acid, and the almost anhydrous acid with the selenium have passed over, pure oil of vitriol is obtained on changing the receiver. When English oil of vitriol is used, it is often necessary, before distilling, to remove the nitric oxide and the arsenic by the preceding methods. When the excess of water with which the hydrochloric acid, nitric acid, &c., may be associated, has passed off, the oil of vitriol may be collected in a fresh receiver. In consequence of the high temperature required for the distillation, the neck of the retort, and the receiver are very apt

to break. The quantity of oil of vitriol distilled in one operation should not exceed 4 pounds. The retort is either immersed in a sand-bath which can be completely surrounded with fire, or else it is exposed to an open charcoal or coke fire, but sunk deep in the furnace, so that the heat may be applied not only to the bottom but all round it. The heat is maintained uniformly at such a degree as to keep the liquid in continuous gentle ebullition. The neck of the retort is either made to reach to the middle of the receiver, so that the heated drops which fall from it may mix at once with the liquid already gone over; or, if it does not pass beyond the neck of the receiver, a long strip of platinum foil is adjusted within the receiver in such a manner, that the acid, as it drops from the mouth of the retort, may run down the metal into the body of the receiver. Closing the joint with paper, luting, &c., is superfluous, and may do harm. The distillation must not be carried to dryness, but only till three-fourths of the liquid has passed over. As the quantity of acid in the retort diminishes, the sulphate of lead dissolved in the common oil of vitriol separates from the liquid, and causes a dangerous percussive ebullition. (I., 276.) The acid remains tranquil for awhile, and then, when a certain amount of heat has accumulated in it, so great a quantity of vapour is suddenly evolved, that not only is the acid projected with violence into the receiver, and the receiver broken by the heat of the liquid suddenly brought in contact with it, but sometimes the elastic force of the vapour is sufficient to burst the upper part of the retort, and scatter the acid all about. Platinum wire or small cuttings of platinum foil counteract this percussive ebullition to a certain extent, as Gay-Lussac has shown. But according to Berzelius (*Lehrb.* 2, 16), their efficacy ceases after awhile; he therefore recommends that the heat be applied only to the sides of the retort, and not at all to the bottom.

Properties of the Mono-hydrated Sulphuric acid. Colourless, transparent, oily liquid, of specific gravity 1·848; freezes at $-25°$ (H. Davy), at $-38°$ in thermometer bulbs (Thomson); boils at 288° (H. Davy), at 327° (Dalton), passing off unaltered, in colourless vapours, which produce a thick white cloud in contact with the air. Does not evaporate in the air at ordinary temperatures. (Bellani.) Inodorous; does not fume. Corrodes organic substances very strongly, and is coloured brown by them.

	Calculation.		H. Davy, Dalton.	Klaproth.	Berthollet.
SO^3	40	81·63	81	74·4	72·675
HO	9	18.37	19	25·6	27·325
HO, SO^3	49	100·00	100	100·0	100·000

Decompositions. 1. When common oil of vitriol of sp. gr. 1·8435 is kept in a retort for several days, at a temperature not quite up to its boiling point, a more dilute acid passes over first, exhibiting on the second day a density of 1·43; then, on the third day, a fuming acid which crystallizes on cooling, distils over (p. 180, *a*); and the residue, which has a density of 1·85, likewise fumes. (C. G. Gmelin, *Pogg.* 2, 419.) A similar observation was likewise made by Julin, (*N. Tr.* 3, 2, 538), and by Hess (*Pogg.* 24, 652), in whose experiment, after 6⅝ lb. of acid out of 10lb. had gone over, an acid containing 13·73 per cent. of water, crystallized in the neck of the retort. (Can it be that, at a certain temperature, $4HO, SO^3$ is resolved into $2HO, SO^3$ and $2HO, 3SO^3$?)—2. Vapour of oil of vitriol passed through a porcelain tube heated nearly to whiteness, is partially decomposed into 2 volumes of sulphurous acid

gas and 1 volume of oxygen. (Gay-Lussac.) — 3. By the electric current it is resolved into oxygen at the positive, sulphur and hydrogen at the negative, pole (I., 452).—4. Vapour of oil of vitriol and hydrogen gas passed together through a red-hot tube, form water, and either sulphurous, sulphuric, or hydrosulphuric acid, according to the proportion of hydrogen present. (Fourcroy & Thénard.)—5. Charcoal decomposes oil of vitriol with the aid of heat. At temperatures between 100° and 150°, the products of the decomposition are carbonic and sulphurous acid; at a red heat, carbonic oxide, carbonic acid, hydrogen, and sulphur. —6. Phosphorus heated with oil of vitriol to the boiling point in a capacious flask, takes fire in the acid vapour and separates the sulphur. Phosphoric oxide, according to Pelouze, does not act on oil of vitriol in the cold, but on the application of heat, phosphoric and sulphurous acids are produced. Phosphuretted hydrogen gas slowly decomposes oil of vitriol at ordinary temperatures, producing phosphoric acid, sulphurous acid, and sulphur. (H. Rose, *Pogg.* 24, 139.) When sulphur and oil of vitriol are distilled together, sulphurous acid passes over, accompanied by sulphuric acid, which is rendered turbid by the presence of sulphur. (F. C. Vogel.) [For the decomposition by hydrosulphuric acid, see that compound.]—8. Potassium and sodium at ordinary temperatures separate nothing but hydrogen from oil of vitriol. Iron and zinc evolve only hydrogen at first; but afterwards, when the temperature rises, they liberate nothing but sulphurous acid gas. Arsenic, tellurium, antimony, bismuth, tin, lead, copper, mercury, silver, and several other metals, exert no action upon oil of vitriol in the cold; but on the application of heat, they cause an evolution of pure sulphurous acid gas. In all these cases, a metallic sulphate is produced, the undecomposed portion of the acid combining with the salifiable base formed by the union of the metal with oxygen derived from the water or from a portion of the sulphuric acid. (*Sch.* 17 and 23.) If zinc be dissolved in dilute sulphuric acid, and, when the temperature of the liquid has risen to about 90°, oil of vitriol be poured in, so that it may lie at the bottom of the vessel in contact with the zinc, hydrosulphuric acid will be evolved: for at the high temperature which the liquid has attained, oil of vitriol and zinc produce sulphurous acid; and this, by the action of the zinc, is further converted into hydrosulphuric acid, (p. 171. Fordos & Gélis, *J. Pharm.* 27, 730.) Some metals, as tungsten, gold, platinum, rhodium, and iridium, do not act on sulphuric acid at any temperature.—9. When oil of vitriol is heated in contact with a fixed base, such as lime, an anhydrous sulphate remains, while the water of the oil of vitriol escapes.

δ. *Bi-hydrated Sulphuric acid.* $2HO, SO^3$. Sometimes called *Glacial Oil* (*Eisöl*). The liquid formed by the union of 1 atom of sulphuric acid and 2 atoms of water, and therefore containing 31 water and 69 acid in 100 parts, has a density of 1·780, solidifies at 9° (48·2° F.), according to Chaptal, and above 7·5 (45·5° F.), according to Dalton, in colourless, transparent, six-sided prisms, terminated by six-sided summits. Between 205° and 210°, this compound loses its second atom of water—a portion of sulphuric acid, however, evaporating at the same time—and leaves oil of vitriol. (Graham.) Graham regards one atom of water as basic,—the other, which is less intimately combined, as constitutional, $HO, SO^3 + HO$.

ε. *Ter-hydrated Sulphuric acid.* $3HO, SO^3$. According to Ure, the combination of 40 pts. (1 At.) of anhydrous sulphuric acid with 27 pts. (3 At.) of water (in which proportions the acid and water contain equal quantities of oxygen) is attended with the maximum degree of conden-

sation. If 49 pts. oil of vitriol and 18 water occupy before mixture the space of 100 measures, they will, after mixture, fill up only 92·14 measures. (Ure.) The specific gravity of this mixture is 1·6321. Between 193° and 199° it loses 1 atom of water, which passes off unaccompanied by acid, the residue having exactly the composition $2HO, SO^3$. (Graham.) This hydrate boils between 163° and 170°. (Liebig.)

ζ *Dilute Sulphuric acid.* Called *Spirit of Vitriol*, when in the proportion of 1 part acid and from 3 to 5 water. Sulphuric acid may be diluted with water in any proportion whatever. According to Gay-Lussac, oil of vitriol placed in an atmosphere saturated with moisture absorbs 15 times its weight of water.

The combination of oil of vitriol with water is attended with great development of heat; but that of oil of vitriol—and still more of δ and ϵ—with snow, produces intense cold. When oil of vitriol is poured into water in successive portions rapidly following one another, and without stirring, phosphorescence is sometimes produced, and lasts for some seconds. (Göbel, *Schw.* 58, 488.) On mixing 4 parts of oil of vitriol with 1 part of water, the temperature rises from 0° to 100°. (Berzelius; *comp.* Hess, I., 294.) One part of oil of vitriol with 1 part of snow evolves heat; with $\frac{1}{4}$ of snow, no change of temperature occurs; and with a larger quantity, intense cold is produced. (Richter.) Bi-hydrated and ter-hydrated sulphuric acid dissolve snow with production of intense cold (I., 299). Sulphuric acid loses, by dilution, its corrosive action on organic substances. Dilute sulphuric acid, when heated, parts with its water, till it is brought to the strength of ordinary oil of vitriol; and this, on being further heated, evaporates unchanged. The compound of 1 atom of anhydrous sulphuric acid with 4 At. water boils between 136° and 141°; and that of 1 At. sulphuric acid with 5 At. water, between 118° and 122°. (Liebig, *Pogg.* 31, 352.) When dilute sulphuric is kept for 40 hours in vacuo at 100°, there remains a compound of 40 pts. (1 At.) of acid with 27·228 (or rather more than 3 At.) water. When the dilute acid is boiled, pure water is given off at first, no acid vapour mixing with the vapour of water till the liquid is brought to the proportion of 2 At. water and 1 At. acid. (Graham.)

Quantity of Oil of Vitriol in Aqueous Sulphuric Acid.

Vauquelin (*Ann. Chim.* 76, 260).			Darcet (*Ann. Chim. Phys.* 1, 198).		
Baume's Areometer.	Spec. Grav.	Oil of Vitriol, per cent.	Baume's Areometer.	Spec. Grav.	Oil of Vitriol, per cent.
66°	1·842	100	66°	1·844	100
60	1·725	84·22	60	1·717	82·34
55	1·618	74·32	55	1·618	74·32
50	1·524	66·45	54	1·603	72·70
45	1·466	58·02	53	1·586	71·17
40	1·375	50·41	52	1·566	69·30
35	1·315	43·21	51	1·550	68·03
30	1·260	36·52	50	1·532	66·45
25	1·210	30·12	49	1·515	64·37
20	1·162	24·01	48	1·500	62·80
15	1·114	17·39	47	1·482	61·32
10	1·076	11·73	46	1·466	59·85
5	1·023	6·60	45	1·454	58·02

Quantities of Anhydrous Acid and Oil of Vitriol in Aqueous Sulphuric Acid.

Anhydrous Acid. Dalton (*N. Syst.* 2, 210).			Anhydrous Acid and Oil of Vitriol. Ure (*Schw.* 35, 444).					
	Percentage.			Percentage.			Percentage.	
Specific Gravity.	Anhydrous Acid.	Boiling Point.		Anhydrous Acid.	Oil of Vitriol.	Specific Gravity.	Anhydrous Acid.	Oil of Vitriol.
1·850	81	326°	1·8485	81·54	100	1·3884	40.77	50
1·849	80	318	1·8460	79·90	98	1·3697	39·14	48
1·848	79	310	1·8410	78·28	96	1·3530	37·51	46
1·847	78	301	1·8336	76·65	94	1·3345	35·88	44
1·845	77	293	1·8233	75·02	92	1·3165	34·25	42
1·842	76	285	1·8115	73·39	90	1·2999	32·61	40
1·838	75	277	1·7962	71·75	88	1·2826	30·98	38
1·833	74	268	1·7774	70·12	86	1·2654	29·35	36
1·827	73	260	1·7570	68·49	84	1·2490	27·72	34
1·819	72	253	1·7360	66·86	82	1·2334	26·09	32
1·810	71	245	1·7120	65·23	80	1·2184	24·46	30
1·801	70	238	1·6870	63·60	78	1·2032	22·83	28
1·791	69	230	1·6636	61·97	76	1·1876	21·20	26
1·780	68	224	1·6415	60·34	74	1·1706	19·57	24
1·769	67	217	1·6204	58·71	72	1·1549	17·94	22
1·757	66	210	1·5975	57·08	70	1·1410	16·31	20
1·744	65	205	1·5760	55·45	68	1·1246	14·68	18
1·730	64	200	1·5503	53·82	66	1·1090	13·05	16
1·715	63	195	1·5280	52·18	64	1·0953	11·41	14
1·699	62	190	1·5066	50·55	62	1·0809	9·78	12
1·684	61	186	1·4860	48·92	60	1·0682	8·15	10
1·670	60	182	1·4660	47·29	58	1·0544	6·52	8
1·650	58·6	177	1·4460	45·66	56	1·0405	4·89	6
1·520	50	143	1·4265	44·03	54	1·0268	3·26	4
1·408	40	127	1·4073	42·40	52	1·0140	1·63	2
1·300	30	115						
1·200	20	107						
1·100	10	103						

Tables of Richter (*Stöchiometrié* 2, 302,) of Dizé (*J. Chim. Med.* 8, 100), of Anthon (J. pr. *Chem.* 7, 70).

¶ Bineau (*N. Ann. Chim. Phys.* 24, 337,) gives the following table of the quantities of oil of vitriol contained in aqueous sulphuric acid of different densities. The numbers marked with a star are those which were determined by direct experiment.

Oil of Vitriol in 100 pts.	Sp. gr. at 0°C.	Oil of Vitriol in 100 pts.	Sp. gr. at 0°C.	Oil of Vitriol in 100 pts.	Sp. gr. at 0°C.
0	1·000	*67·6	1·600	81	1·759
*3·86	1·028	68	1·605	82	1·770
5	1·035	*68·2	1·608	83	1·781
*7·1	1·051	69	1·617	84	1·791
10	1·073	70	1·628	*84·1	1·792
*11·7	1·086	*70·3	1·632	85	1·800
15	1·112	71	1·640	86	1·808
*17·5	1·131	*71·3	1·643	*86·6	1·813
20	1·151	*71·7	1·648	87	1·816
*21·4	1·162	72	1·652	88	1·823
25	1·192	*72·9	1·663	*88·4	1·828
30	1·232	73	1·664	90	1·830
*32·2	1·250	*73·1	1·666	91	1·836
35	1·274	*73·3	1·6675	92	1·841
40	1·317	74	1·676	93	1·845
*42·2	1·336	*74·2	1·6775	93·5	1·848
45	1·362	*74·7	1·685	94	1·8495
*48·9	1·399	75	1·688	*94·5	1·850
50	1·410	*75·5	1·6935	95	1·851
55	1·460	76	1·700	96	1·852
56·4	1·475	77	1·712	*97·0	1·853
60	1·514	78	1·724	98	1·8545
*63·4	1·553	*78·4	1·729	*98·5	1·855
65	1·570	79	1·736	99	1·8564
66	1·581	80	1·748	100	1·857
67	1·593	*80·2	1·750		

If it be required to determine by this table the quantity of oil of vitriol contained in a sample of acid, the specific gravity of which has been taken at any temperature above zero, a correction will be required to bring the density to the standard temperature. For this purpose the following data are given:

Specific Gravity of the Acid at 0°C.	Decrease of the Spec. Grav. by a rise of temp. = 10° C. or 18° F.
1·04	0·002
1·07	0·003
1·10	0.004
1·15	0·005
1·20	0·006
1·30	0·007
1·45	0·008
1·70	0·009
1·85	0·0096

According to the foregoing table, the maximum of condensation is found, not in the combination of 1 At. sulphuric acid with 3 At. water, but in the mixture which contains 75·5 parts of HO, SO^3 in 100 parts of liquid. ¶

b. With Boron?—*c.* With Boracic acid.—*d.* With Phosphuretted Hydrogen.—*e.* With Nitric oxide.

f. With Salifiable Bases. *Sulphates, Vitriols, Schwefelsaure Salze.* Of all acids, sulphuric acid has the strongest affinity for the greater number of salifiable bases; it is therefore employed to separate many other acids from their combinations with bases.—Oil of vitriol will not combine with baryta unless heat be applied; the anhydrous acid, on the contrary, and likewise the hydrated acid, when it contains either more

or less water than oil of vitriol, combines rapidly with baryta, even at ordinary temperatures. (*Vid.* Barium.) The vapour of anhydrous sulphuric acid, or of oil of vitriol exerts scarcely any decomposing action on calcspar. (*Vid.* Calcium.) Oil of vitriol mixed with 6 parts of absolute alcohol neither reddens litmus nor decomposes any anhydrous carbonate; but it decomposes acetates with facility. (*Vid.* Alcohol.)—The combination of sulphuric acid with salifiable bases is attended with considerable evolution of heat, sometimes rising even to ignition: *e. g.* with baryta and magnesia.

There exist mon-acid, bi-acid, and ter-acid, besides a few basic sulphates. The normal salts of the alkalis, magnesia, protoxide of manganese, and oxide of silver, are neutral; the rest redden litmus. The normal salts which contain a volatile base (ammonia) are decomposed at a red heat; those which contain a fixed base, and are held together by a strong affinity, are unaltered by ignition (fixed alkalis, magnesia, oxide of lead.) When, on the other hand, the affinity between the acid and base is weaker, water, if present, is first driven off,—and then the anhydrous sulphuric acid is evolved, partly in the unaltered state, partly in the form of sulphurous acid and oxygen (sulphates of antimony, zinc, copper, and ferric oxide);—or if the affinity be so weak as to allow of the volatilization of the acid before all the water is driven off, oil of vitriol is evolved (sulphate of gold). A very high temperature is required to separate the last portions of sulphuric acid from the oxides of zinc, cadmium, cobalt, nickel and copper.—If the base has a tendency to take up more oxygen (ferrous oxide), it abstracts oxygen at high temperatures from the sulphuric acid, thereby converting it into sulphurous acid; the oxides of the noble metals, on the contrary, give up their oxygen, and are reduced to the metallic state.

All sulphates are decomposed by ignition with charcoal. Treated in this manner, sulphate of magnesia,—and likewise sulphate of zinc, at a moderate heat—are resolved into metallic oxide, and a mixture of two measures of sulphurous acid and one of carbonic acid gas.

$$2\,(MgO, SO^3) + C = 2MgO + 2SO^2 + CO^2.$$

The sulphates of bismuth, silver, and protoxide of mercury—and at a gentle heat also the sulphate of copper—are resolved into reduced metal and equal volumes of sulphurous and carbonic acid gases:

$$AgO, SO^3 + C = Ag + SO^2 + CO^2;$$

Sulphate of lead, and at a strong heat, also the sulphates of copper and zinc, are resolved into metallic sulphide and carbonic acid gas.

$$PbO, SO^3 + 2C = PbS + 2CO^2;$$

and sulphate of manganous oxide, into oxysulphide of manganese and 1 volume of sulphurous acid gas, together with 3 volumes of carbonic acid

$$4\,(MnO, SO^3) + 5C = 2\,(MnS, MnO) + 2SO^2 + 5CO^2?$$

(Gay-Lussac.) The fixed alkaline sulphates are reduced in a similar manner to sulphate of lead, at least at a white heat (Berthier, *Ann. Chim. Phys.* 22, 229), monosulphide of the metal and carbonic acid gas being produced;—but the latter is more and more replaced by carbonic oxide, in proportion to the quantity of charcoal with which the sulphate has been mixed. (Clement & Desormes, *Gilb.* 9, 422.) At a red heat, on the contrary, part of the alkali remains undecomposed—the quantity being greater as the temperature is lower—and a sulphide is produced con-

taining more than 1 atom of sulphur to 1 atom of metal, and consequently forming a yellow solution when dissolved in water. (Gay-Lussac, *Ann. Chim. Phys.* 30, 24.) Sulphates fused with carbonate of soda upon charcoal before the blow-pipe yield a mass which contains sulphide of sodium, and when moistened with water and placed upon silver foil, blackens it immediately; it also evolves sulphretted hydrogen when treated with acids. (Smithson.) Fused upon charcoal with carbonate of soda and glass (or silica) they form a bead which is colourless or dark brown while hot, but on cooling acquires a red or yellow tint,—and if much sulphide of sodium is present, becomes opaque. (Gahn.) Both these reactions are likewise exhibited by the salts of hyposulphurous, pentathionic, tetrathionic, trithionic, sulphurous, and hyposulphuric acid.

On passing hydrogen gas through a red hot tube containing an inorganic sulphate, water is produced, together with either a metallic sulphide (as in the case of potassa, *Sch.* 84), or a compound of sulphide and oxide (*e. g.* protoxide of manganese. Arfvedson, *Pogg.* 1, 49), or an oxide alone (magnesia).

Boron and phosphorus act in the same manner as carbon and hydrogen, sometimes with formation of a borate or phosphate. Sulphates are also decomposed by potassium, sodium, manganese, antimony, zinc, tin, and iron.

¶ Sulphate of potassa is completely decomposed by igniting it for a short time with finely divided iron. A blackish porous mass is obtained, consisting of sulphide and oxide of iron and caustic potassa.

$$KO, SO^3 + 3Fe = KO + Fe^2O^3 + FeS$$

The same salt ignited with excess of zinc, yields a compact lemon-yellow coloured mass consisting of sulphide of potassium and oxide of zinc.

$$KO, SO^3 + 4Zn = KS + 4ZnO$$

Sulphate of soda exhibits similar reactions. When a solution of sulphate of ammonia is boiled in contact with iron, ammonia is evolved, and the solution is afterwards found to contain a salt of ferrous oxide. On fusing the mixture at a gentle heat, the evolution of ammonia is stronger and the salt assumes a dark colour, and gives a greenish solution in water. If the mixture be suddenly heated to redness, sulphurous acid escapes together with the vapour of the salt, and the surface of the iron becomes covered with sesqui-oxide, and sometimes also with sulphide. These products appear however not to be formed directly, but to result from the decomposition of ferrous sulphate produced by the fusion. Zinc exhibits similar results. Sulphate of lime ignited with iron in a porcelain crucible yields a greyish black mass of metallic aspect, containing sulphide of calcium and an oxide of iron. The two following reactions appear to take place at the same time:

$$(1.)\ CaO, SO^3 + 3Fe = CaS + Fe^3O^4$$
$$(2.)\ 3CaO, SO^3 + 8Fe = 3CaS + 4Fe^2O^3$$

Sulphate of lime ignited with pure zinc yields a yellowish scaly mass containing lime, together with oxide and sulphide of zinc, but no sulphide of calcium:

$$CaO, SO^3 + 4Zn = CaO + 3ZnO + ZnS.$$

The sulphates of baryta and strontia give similar results: a higher temperature is however required for the decomposition of sulphate of strontia by iron. Sulphate of magnesia ignited with iron evolves a considerable quantity of sulphurous acid, and forms a mass having an iron-grey aspect

and containing white lumps of magnesia here and there. The iron is converted into protoxide and sesqui-oxide with a portion of sulphide. In these decompositions it is especially remarkable that, in those cases in which the iron takes up both constituents of the sulphuric acid, the zinc combines only with the oxygen; and where the zinc is converted into both oxide and sulphide, the iron does not enter into combination with the sulphur, but only with the oxygen. (Albert d'Heureuse, *Pogg.* 75, 255.) ¶

Dilute aqueous solutions of alkaline sulphates are converted into alkaline hydrosulphates or metallic sulphides by organic substances dissolved in or diffused through them. (Kastner, *Kastn. Arch.* 1, 360.) The sulphur gives it up its oxygen to the carbon and hydrogen of the organic substance, and takes hydrogen from it; or, on the other hypothesis, the sulphuric acid and alkali are both deprived of their oxygen. A solution of sulphate of soda in about 500 parts of water, or a saturated solution of gypsum, mixed with a little sugar, gum, or glycyrrhizin, and kept from half a year to two years in a close vessel, is found to contain hydrosulphuric, carbonic, and acetic acid, the two former partly free, partly in combination with soda or lime. This explains the occurrence of acetic acid in many mineral waters. A peculiarly rapid decomposition has been found to be produced by water which has stood for six months in contact with beechwood. (A. Vogel, *Kastn. Arch.* 15, 306.) A piece of straw placed in a vessel filled with a mineral water, develops hydrosulphuric acid, if the air has access to the liquid (the air probably facilitating the decomposition of the straw), but not if the air is completely excluded. Many mineral waters already contain organic matter in solution, so that the addition of such matter to them is superfluous. (Kastner.) Such is the case with the gypsum-water of Berka. (Döbereiner, *Schw.* 8, 461.) Water from Passy, which contains sulphate of lime and other sulphates, together with organic matter, was found, after being kept for a year in jugs placed in a cellar, to be rich in hydrosulphuric acid; and all the ferrous carbonate which it contained, was converted into a black powder, consisting of monosulphide of iron (or ferrous hydrosulphate); slimy flakes of an azotized organic substance were likewise found in it. (O. Henry, *J. Pharm.* 13, 208.) Gypsum from the neighbourhood of Paris, which is thoroughly impregnated with organic matter, develops hydrosulphuric acid when placed in bottles with water. (O. Henry, *J. Pharm.* 22, 596.) The formation of hydrosulphuric acid in mineral waters which have been kept for some time in contact with organic matter is likewise confirmed by Bischof (*Schw.* 57, 80.) Many sulphur-springs doubtless derive their hydrosulphuric acid from the decomposition of alkaline sulphates by organic matter taking place in the earth. The alteration which takes place by long keeping in a wet mass of porcelain clay containing gypsum and organic matter, may likewise be explained in the same manner. In hot climates, as on the West Coast of Africa, where the water of the rivers highly charged with organic matter, mixes with the sea-water which contains salts of sulphuric acid, the same decomposition takes place—extending sometimes to a distance of 27 miles from the mouths of the rivers. The water contains hydrosulphuric acid, sometimes as much as six cubic inches in a gallon; hence it exerts a peculiarly rapid action on the copper sheathing of ships, and its evaporation gives rise to malignant fevers. The same miasma is produced when seawater mixes with fresh water upon land. According to Daniell, the hydrosulphuric acid itself is the miasma; hence chlorine is efficacious in de-

stroying it. (*Ann. Chim. Phys.* 78, 331.) But if that were the case, chemists, as well as persons living in the neighbourhood of sulphur-springs would be often attacked with malignant fevers. The presence of hydrosulphuric acid may however facilitate the development of the miasma, which is undoubtedly something organic. (*Gm.*)

Many fixed acids, as phosphoric, boracic, and silicic acid, though endued with less affinity than sulphuric acid has for salifiable bases, nevertheless decompose sulphates at various degrees of ignition, combining with the base of the salt and expelling the sulphuric acid, sometimes unaltered, sometimes resolved into sulphurous acid and oxygen. Hydrochloric and nitric acid deprive the normal sulphates of ammonia, potassa, and soda of half their base, giving rise to the formation of an alkaline bisulphate. (I., 126, 127.) On the other hand, the sulphates of magnesia, alumina, oxide of zinc, protoxide of iron, oxide of nickel and protoxide of mercury, crystallize unaltered from solution in hydrochloric acid; and hydrochloric acid gas passed over dry sulphate of potassa, soda, magnesia, alumina, oxide of zinc, oxide of lead or protoxide of iron, exerts no action;—the sulphates of oxide of nickel and protoxide of mercury absorb half an atom of hydrochloric acid, which is evolved on the application of heat and likewise extracted by water.

The normal sulphates of sesqui-oxide of antimony, protoxide of bismuth, protoxide of mercury, and di-oxide of mercury are resolved by contact with water into dilute acid and residual basic salts. The sulphates of magnesia, zinc and nickel and the protosulphates of manganese, iron, cobalt and copper, which crystallize in combination with water, retain one atom of their combined water, the *saline* or *constitutional water*, (II., 65) much more strongly than the remaining atoms, not parting with it in fact, till they are heated to 204° (400° F.). This atom of water is likewise separated at lower temperatures by the introduction of another salt of sulphuric acid, which forms a double salt with the former: *e. g.* $ZnO, SO^3 + HO$ is converted by KO, SO^3 into $ZnO, SO^3 + KO, SO^3$, the water being liberated; hence it appears that the constitutional water plays the part of a salt. (Graham, *Phil. Mag. J.* 6, 329; also *J. pr. Chem.* 6, 50.—*Ann. Pharm.* 29, 27.) All bisulphates and tersulphates are either soluble in water, or are resolved by it into hydrated sulphuric acid and a simple salt. Basic sulphates are insoluble in water, but soluble in dilute hydrochloric acid. Normal sulphates are mostly soluble in water; the lime and silver salts however are but slightly soluble, and the strontia, baryta, and lead salts scarcely at all; moreover, their solubility is not sensibly increased by the addition of sulphuric acid to the water. The sulphates of baryta and strontia, on the contrary, are soluble to a considerable extent in oil of vitriol, and precipitated from the solution on the addition of water.

All soluble sulphates, as well as basic sulphates dissolved in hydrochloric acid, give with soluble salts of baryta, a white precipitate, insoluble in dilute nitric or hydrochloric acid. A solution of sulphate of potassa, containing one part of sulphuric acid in 50,000 parts of water, gives a slight turbidity with nitrate of baryta, and very slight with nitrate of lead; with 1 part of acid in 100,000 of water, the former reagent gives a very slight turbity, the latter none; with the same quantity of salt in 200,000 parts of water, nitrate of baryta gives a very slight cloudiness after the lapse of 15 or 20 minutes; and in 400,000 parts of water, none at all. (Lassaigne, *J. Chim. Med.* 8, 522.) When sulphates, insoluble in water, are boiled in solution of carbonate of soda, the filtered liquid super-

saturated with hydrochloric acid likewise precipitates baryta salts. Most sulphates are insoluble in alcohol.

g. With many organic substances.

Sulphur and Hydrogen.

A. Hydrosulphurous Acid. HS^5.

Persulphide of Hydrogen, Wasserstoff-schwefel, Wasserstoff-supersulfür Hydrothionige Säure, Hydrure de soufre, Soufre hydrogéné.

Formation. Under the following circumstances, solutions are formed which may be supposed to contain either an alkaline hydrosulphite or a pentasulphide of the corresponding metal: 1. When pentasulphide of potassium or sodium is dissolved in water:

$$KS^5 + HO = KO, HS^5.$$

2. When the aqueous solution of the monosulphide of an alkali-metal, or —what comes to the same thing—an alkaline hydrosulphate, is digested with sulphur, of which it dissolves 4 atoms:

$$KS + 4S = KS^5\text{: or: } KO, HS + 4S = KO, HS^5.$$

3. When a solution of the kind just mentioned is exposed to the air (vid. *Metallic Sulphides*).—4. When sulphur is boiled with the aqueous solution of a fixed alkali, a hyposulphite being formed at the same time:

$$3CaO + 12S = 2CaS^5 + CaO, S^2O^2;$$
$$\text{or: } 3CaO + 12S + HO = 2\,(CaO, HS^5) + CaO, S^2O^2.$$

5. Hydrosulphite of ammonia appears to be sometimes produced in the putrefaction of organic substances containing sulphur.

Preparation. 1. A concentrated solution of pentasulphide of potassium, obtained by fusing carbonate of potassa with excess of sulphur, is poured by small portions at a time into a lukewarm mixture of hydrochloric acid and water. (Berzelius.)

$$KS^5 + HCl = KCl + HS^5.$$

To obtain pentasulphide of potassium, Liebig heats 2 parts of carbonate of potassa with 1 part of sulphur to a state of red-hot fusion, dissolves the fused mass when cool in water, saturates the solution at a boiling heat with sulphur, and filters.—2. One part of lime burned and slaked, is boiled with 2 parts of sulphur and 16 of water; and this solution, after cooling and filtering, is poured into an excess of dilute hydrochloric acid. Thénard boils the lime for a considerable time with excess of sulphur, and pours the filtrate slowly, stirring all the while, into a mixture of one part commercial hydrochloric acid and 2 parts water. Liebig boils one part of lime and 1 part of sulphur in 16 parts of water, and pours the filtrate at once into half its bulk of a mixture of 2 parts fuming hydrochloric acid and 1 part water. Since the hydrochloric acid decomposes not only the pentasulphide of calcium or hydrosulphite of lime, but likewise the hyposulphite of lime, and since the hyposulphurous acid thus set free is gradually resolved into sulphurous acid and sulphur, the sulphur necessarily becomes mixed with the precipitated hydrosulphurous acid. Hence, according to Thénard, the portions of hydrosulphurous

acid first precipitated are more fluid than those which are deposited afterwards.

In both modes of preparation, the hydrosulphurous acid separates in fine drops, which produce a milky turbidity in the liquid, and collect at the bottom in the form of an oily liquid. Thénard performs the precipitation in a funnel, the neck of which is furnished with a stopper, so that the precipitated acid may be let out at pleasure.

Properties. Yellow, transparent, oily, liquid, having the consistence of thin oil, when it contains a minimum quantity of sulphur, and that of a viscid oil, when the quantity of sulphur is larger: in the latter case, its density is 1·789. (Thénard.) It has a peculiar, sulphurous, disagreeable odour, and irritates the nose and eyes. Tastes sweet and bitter, and imparts a white colour to the tongue and saliva. A few drops placed upon the skin of the arm, alter and decolorize it. (Thénard.) At the moment of its precipitation, according to method 2, it bleaches litmus paper introduced into the milky liquid. (Thénard.)

Calculation.			Or:		
5S	80	98·76	4S	64	79·01
H	1	1·24	HS	17	20·99
HS^5	81	100·00	HS^5	81	100·00

(H^2S^5 = 2 . 6·24 + 5 . 201·17 = 1018·33. Berzelius.)

In consequence of the excess of sulphur always mixed with this compound, analysis gives 6 or 8 atoms of sulphur instead of five. (Thénard.)

Decompositions. 1. The acid, if left to itself for a few days, is resolved into hydrosulphuric acid, which escapes as gas, and sulphur, which remains behind, so that the liquid becomes more and more viscid, and ultimately solid. The decomposition is more rapid at 60°, and still more so at 100°. (Thénard.) Even when this compound is sealed up in a glass tube, it resolves itself completely, in the course of three weeks, into transparent crystals of sulphur and colourless liquid hydrosulphuric acid. (Kemp, *Phil. Mag. J.* 7, 444; also *Ann. Pharm.* 28, 170; Liebig.) The decomposition in the sealed tube, however, does not take place unless water is present; so that by adding a little chloride of calcium to the hydrosulphurous acid, it may be kept in the tube unaltered. (Bunsen, *Pogg.* 46, 103.) Acids prevent the decomposition: the liquid, when immersed in hydrochloric acid, will remain for a long time in open vessels without alteration. Even on boiling it with the aqueous solution of an acid, the decomposition takes place very slowly; and after the greater part of the hydrosulphuric acid has escaped, the vapours exert a peculiar irritating action on the nose and eyes. (Berzelius.) On the other hand, decomposition is accelerated by the following substances: *a.* Finely divided charcoal, silica, manganese, kermes-mineral, galena, sulphide of gold, gold, platinum, and other metals; also by sugar, starch, and lignin, which however exert but a very feeble action. (Thénard.) Silica and kermes-mineral, in the state of powder, produce a slight disengagement of gas at the particular points in which they touch the liquid; but if previously wetted, they do not produce this effect. (Liebig.)—*b.* Pentasulphide of potassium, either in solution or diffused through water, causes a very violent evolution of hydrosulphuric acid gas, and sudden precipitation of sulphur. (Thénard.) Alcoholic solution of liver of sulphur likewise effects the decomposition, without evolution of hydrosulphuric

acid. (Liebig.)—*c*. Decomposition is also brought about by powdered hydrate of potassa, baryta, strontia, lime, or magnesia; likewise by aqueous solution of ammonia or potassa. (The potassa, according to the earlier observation of Berzelius, is thereby converted into sulphide of potassium, or hydrosulphate of potassa.) These substances perhaps form metallic sulphides in the first instance, and the sulphides exert the decomposing action. (Thénard.) With a small quantity of solution of potassa, hydrosulphurous acid evolves sulphuretted hydrogen gas: with an excess of the alkali, it is at once converted into soft spongy sulphur, which evolves but few bubbles of gas. In excess of aqueous solution of ammonia, it is immediately converted, with frothing and decrepitation, into brittle, blistered sulphur; the liquid is found to contain sulphide of ammonium, with more than 1 atom of sulphur. (Liebig.)—*d*. Mixed with finely pounded chloride of calcium, it froths up violently and becomes solid after a time. Effloresced Glauber's salt acts more slowly; the same salt in the crystallized state, not at all. Some of the above-mentioned substances probably act by abstracting water. (Liebig.)—*e*. Water agitated with hydrosulphurous acid, takes hydrosulphuric acid from it, and becomes milky. Alcohol appears to act in a similar manner. Ether dissolves it at first, but soon deposits white acicular crystals of sulphur, which become yellow when dry.

2. Hydrosulphurous acid may be set on fire by the flame of a candle, and burns with a blue flame.

3. Oxide of silver and oxide of gold placed in contact with this substance, become red hot, water being formed, and the oxide reduced to the metallic state. (Thénard.) Oxide of silver is converted into sulphide. (Liebig.)

Combinations. Hydrosulphurous acid appears to be insoluble in water. It combines with certain salifiable bases? forming salts, called *Hydrothionites*. (Vid. *Metallic Sulphides*.)

B. Hydrosulphuric Acid. HS.

Sulphuretted Hydrogen, Sulphide of Hydrogen, Hydrothionsäure, Hydrothion, Hydrogène Sulfuré, Acide hydrosulphurique, Acide sulfhydrique, Sulfide hydrique, Hydrogenium sulphuratum; and in the gaseous state: *Hydrosulphuric acid gas, Sulphuretted Hydrogen gas, Hepatic air, Hydrothionsaures Gas, Hydrothion Gas, Schwefelleberluft, Gas hydrogène Sulfuré, Gas hydrogenium sulphuratum.* Exists in hepatic waters, in sea-water near the mouths of certain rivers (II. 192), in putrid eggs, and in sewers.

Formation. 1. When sulphur is heated to the subliming point for a considerable time in hydrogen gas, or when hydrogen is passed over melted sulphur, combination takes place between the two, but very slowly and imperfectly, so that, even after the process has been continued for a long time, a considerable quantity of hydrogen remains uncombined. The volume of the gas remains unaltered. (Scheele, H. Davy.)—2. On bringing various metallic sulphides in contact with dilute acids, the metal takes oxygen from the water, and forms an oxide which dissolves in the acid, while the hydrogen of the water enters into combination with the sulphur:

$$FeS + HO + SO^3 = FeO,SO^3 + HS.$$

In the case of hydrogen acids, it is simpler to suppose that the radical of the acid is transferred to the metal and its hydrogen to the sulphur; thus:

$$FeS + HCl = FeCl + HS.$$

3. When organic compounds containing sulphur putrefy or are heated by themselves; or when other organic compounds are heated in contact with sulphur. If the existence of hydrogen-salts of metallic oxides be admitted, it must likewise be supposed that hydrosulphuric acid is generated when a monosulphide of an alkali-metal is dissolved in water, and when iron filings are mixed with water and sulphur.

Preparation. 1. *In the gaseous state:—a.* Oil of vitriol diluted with about eight times its quantity of water, either at the temperature of the air or a little above it, is put into a gas-generating vessel (App. 40), together with one of the following substances: *Monosulphide of iron:* this substance evolves the gas slowly and continuously, but generally mixed with hydrogen: *Hydrated Monosulphide of iron,* or *hydrosulphate of protoxide of iron,* prepared by heating for a short time, and out of contact of air, a mixture of 1 part flowers of sulphur, 2 parts iron filings, and a quantity of water sufficient to make it into a paste (Tourte, *Berl. Jahrb.* 18, 202; Gay-Lussac, *Ann. Chim. Phys.* 7, 314): evolves the gas very rapidly, and generally mixed with free hydrogen, the action is soon over; this hydrated sulphide cannot be kept long. *Sulphide of calcium,* prepared by igniting 3 parts of gypsum with 1 part of charcoal, in a covered crucible: evolves the gas rapidly and in abundance; cannot be kept very long. *Potash liver of sulphur* (the old method). *Impure sulphide of manganese,* obtained by igniting 6 parts of sulphate of manganese with 1 part of charcoal (Berthier), or 5 parts of ignited oxide of manganese with 2 parts of sulphur and 1 part of charcoal: evolves the gas very rapidly; spoils by long keeping. *Sulphide of iron and sodium,* prepared by fusing 2 parts of iron pyrites with 1 part of anhydrous carbonate of soda. (Berthier.)—*b.* By heating tersulphide of antimony with concentrated hydrochloric acid; the gas is not evolved in very large quantity, but it is free from hydrogen.—*c.* By heating in a glass flask a mixture of equal parts of sulphur and beef-suet. By this method, the gas is obtained pure and with slight frothing; when it is wanted for use, the flask is to be heated. (Reinsch, *J. pr. Chem.* 13, 142.)

Hydrosulphuric acid gas is collected over warm water or brine, which absorb less of it than pure cold water,—or over mercury.

2. *In the liquid state: a.* Faraday's method. (I., 286.) The sulphide of iron must be freed from uncombined iron by repeated ignition with sulphur; otherwise, free hydrogen will be disengaged and the tube will be burst. (Niemann, *Br. Arch.* 36, 189.)—*b.* Persulphide of hydrogen enclosed in a sealed tube gradually resolves itself into sulphur and hydrosulphuric acid, the latter assuming the liquid state. (Kemp; Liebig; Bunsen, II. 194.)

¶ 3. *In the solid state:* By Faraday's process (I., 287.) solidification takes place at—122°. Fah.

Properties. 1. In the solid state: White, crystalline, translucent substance, heavier than the liquid; it occupies the same place in the sulphur series of compounds that ice does in the oxygen series. ¶

2. *In the liquid state:* Colourless, transparent liquid, much thinner

and less adhesive than ether; specific gravity about 0·9; refracting power higher than that of water. Does not solidify at − 17·8°. (Faraday: *see above*.) The thinnest of all liquids; refracts light more strongly than sulphurous acid or ammonia. With the aid of heat it dissolves sulphur, which, on cooling, crystallizes out in yellow warty masses. (Niemann.)

3. *In the gaseous state:* Tension, sp. gr. and refractive power of the gas (I., 261, 279, and 95). Colourless. Smells like rotten eggs, and produces fainting and asphyxia, even when mixed with the air in very small quantity: when inhaled in the pure state, it acts as a powerful narcotic poison. Does not support combustion, but is itself inflammable. Reddens tincture of litmus; the reddening disappears on exposure to the air.

	Calculation.		Berzelius. earlier.	Berzelius. later.	Thénard & Gay-Luss.	Thénard (earlier.)
S	16	94·1	93·8	94·176	93·855	70·857
H	1	5·9	6·2	5·824	6·145	29·143
HS	17	100·0	100·0	100·000	100·000	100·000

	Vol.	Sp. gr.		Vol.	Sp. gr.
Sulphur vapour	1	6·6556	=	$\frac{1}{6}$	1·1093
Hydrogen gas	6	0·4158	=	1	0·0693
Hydrosulph. acid gas	6	7·0714	=	1	1·1786

($H^2S = 2 . 6·24 + 201·17 = 213·65$. Berzelius.)

Decompositions. 1. Hydrosulphuric acid gas, passed through a red-hot porcelain tube, is converted into pure hydrogen gas, with deposition of sulphur. (Cluzel, *Ann. Chim.* 84, 166.)—2. Two platinum wires made to form the poles of a powerful voltaic battery, and kept in a state of ignition in this gas, produce the same action: the electric spark likewise acts in the same manner, but much more slowly. The volume of the gas remains unaltered. (H. Davy.)

3. Hydrosulphuric acid gas burns in contact with air or oxygen under the same conditions as hydrogen gas. It may be inflamed by charcoal or iron, even at a low red heat. (H. Davy.) In the air it burns with a blue flame, forming water and sulphurous acid, and depositing sulphur; mixed with oxygen gas, it burns with explosion. One volume of hydrosulphuric acid gas exploded with half a volume of oxygen, is completely converted into water and sulphur, because half a volume of oxygen is exactly sufficient to convert the 1 volume of hydrogen contained in 1 volume of hydrosulphuric acid gas into water: with $1\frac{1}{2}$ vol. oxygen, it is completely converted into water, and 0·87 vol. (in reality 1 vol.) of sulphurous acid gas. (Dalton.) In this case, 1 vol. oxygen gas combines with $\frac{1}{6}$ vol. sulphur vapour to form 1 vol. sulphurous acid gas: part of this, however, is absorbed by the water which is formed at the same time.—If the mouth of a flask in which hydrosulphuric acid is generated be connected with that of an inverted flask, the bottom of which has been removed, so that a mixture of air and sulphuretted hydrogen may be formed in it, this mixture may be inflamed by a red-hot coal, burning tinder, red-hot iron, lava, &c., but not by ignited zinc, copper, or glass. The combustion is attended with the production of a thick white cloud, which spreads out from the ignited body throughout the whole mixture. The products are, water, sulphurous acid, and sulphur. Similar fumes, but extending to the distance of several feet,

are formed at the fumaroles of Agnano, near Naples, on the approach of a piece of lighted tinder, these fumaroles evolving hydrosulphuric acid gas. (Piria, *Ann. Chim. Phys.* 74, 331.) Spongy platinum does not ignite a mixture of hydrosulphuric acid and oxygen; but if hydrogen be likewise present, the spongy platinum becomes ignited in the detonating gas, and then sets fire to the sulphuretted hydrogen. (Döbereiner.) Platinum-paper-ash or palladium-paper-ash must be heated to about 100° before it will attain a red heat in a stream of sulphuretted hydrogen; it then sometimes sets the gas on fire. As sulphur is in that case deposited upon the ash, it must be cleaned with nitric acid before it will act again. (De la Rive & Marcet.) A ball of platinized clay slowly condenses a mixture of hydrosulphuric acid and oxygen, with formation of water, and deposition of sulphur on the platinum ball, by which it is gradually deprived of its activity. In a mixture of equal measures of hydrosulphuric acid, hydrogen, and oxygen, the platinum ball, during the first 24 hours, induces the oxygen to combine only with the hydrogen contained in the hydrosulphuric acid, the free hydrogen not entering into combination with the oxygen till afterwards. (Graham, *N. Qu. J. of Sc.* 6, 354.)

¶ The oxidation of sulphuretted hydrogen in the air is sometimes attended with the formation of sulphuric acid; the presence of water appears however to be essential to the production of this result. Dumas (*N. Ann. Chim. Phys.* 18, 502) found that when pieces of linen or cotton were placed in a glass tube, and sulphuretted hydrogen mixed with air passed through the tube, no sulphuric acid was formed at ordinary temperatures, if the gases and the linen were dry; but if the linen were wetted, sulphuric acid was produced. On heating the wet linen to 40—50° C. (and still more, if it were heated to 80° — 90°) considerable quantities of sulphuric acid were formed in the course of fifteen or twenty minutes,—so that when the linen was afterwards soaked in water, the water acquired an acid reaction and gave a strong cloud with chloride of barium. The formation of sulphuric acid in this way is observed at the baths of Aix in Savoy. The walls of these baths, which are built of limestone, become covered after a while with crystals of gypsum; and iron hooks fixed in the doors are soon converted into green vitriol. Linen immersed in the water quickly becomes inpregnated with sulphuric acid, —and, in the course of a few weeks, is so strongly attacked by it, as to fall to pieces on being dried and rubbed. Now, as the vapours of these baths contain no sulphuric acid, and do not even redden litmus, the effects just described can only be accounted for by the oxidation of sulphuretted hydrogen contained in the water. Phenomena of the same kind are often observed in volcanic districts. The vapours which issue from the fumaroles of Tuscany contain small quantities of sulphuretted hydrogen, but no free sulphuric acid: nevertheless, when they come in contact with the soil, they convert the carbonate of lime therein contained into sulphate. Humboldt & Boussingault have also found free sulphuric acid in the water of the Rio de Pasambio, not very far from the volcano of Purace in South America. (*Ann. Pharm.* 60, 187.) ¶

4. Oxygenised bodies decompose hydrosulphuric acid, chiefly by oxidating the hydrogen. *a.* Sulphurous acid gas mixed with twice its volume of hydrosulphuric acid gas in the moist state (according to Cluzel, no action takes place when the gases are dry) condenses to a yellow substance which may be regarded as a mixture of water and sulphur (*Sch.* 69). Thomson (*Ann. Phil.* 12, 441) regards this substance as sulphite of sulphuretted hydrogen.—*b.* When hydrosulphuric acid gas is passed

through oil of vitriol, water is formed together with a portion of sulphurous acid, and sulphur is deposited. According to Döbereiner (*Schw.* 13, 481) this takes place only with the Nordhausen acid: according to A. Vogel (*J. pr. Chem.* 4, 232), the same action is also produced with rectified oil of vitriol, and likewise, though slowly, in a mixture of the latter with $\frac{1}{4}$ water, but not in a mixture of 1 pt. oil of vitriol and 4 pts. water; in the latter case, no turbidity is produced unless sulphurous acid, arsenious acid, &c. be present.—*c*. Sulphuretted hydrogen takes fire in hypochlorous acid gas, and by contact with concentrated nitric acid. With peroxide of hydrogen, its aqueous solution is resolved into water and sulphur;—with selenious acid, into water and selenide of sulphur;—with iodic acid, into water, sulphur, and iodine;—with alkaline iodates, into water, sulphur, sulphuric acid, and iodine;—with bromic acid, into water, sulphur, and bromine; with alkaline bromates, into water, sulphuric acid, and bromine; with excess of hypochlorous acid, into water, sulphuric acid, chlorine, and hydrochloric acid;—with nitric acid and certain nitrates, into water, sulphur, sulphuric acid, nitric oxide, and ammonia;—with alkaline chromates mixed with acetic acid, into water, sulphur, and chromic oxide; and with the aid of heat, sulphuric acid also. (See these acids.)—*d*. In contact with hydrosulphuric acid at ordinary temperatures, many metallic oxides, even when combined with acids, are resolved by double decomposition into water and metallic sulphides; with others, the change does not take place till heat is applied (*Sch.* 41, 42, 43, 44). Ferric oxide dissolved in acids is reduced to ferrous oxide, with formation of water and precipitation of sulphur,—and sometimes, if the liquid be heated, with formation of sulphuric acid.

5. With one atom of iodine, bromine, or chlorine, hydrosulphuric acid yields hydriodic, hydrobromic, or hydrochloric acid gas, and sulphur; the latter may, by an excess of these bodies, be converted into iodide, bromide, or chloride of sulphur. If water be likewise present, iodine in excess produces sulphuric acid, provided the temperature be raised (H. Rose, *Pogg.* 47, 161); but chlorine produces that acid abundantly. Terchloride of phosphorus and hydrosulphuric acid produce hydrochloric acid and tersulphide of phosphorus. (Serullas.)

6. Heated potassium or sodium absorbs the whole of the sulphur and one volume of hydrogen from 2 volumes of hydrosulphuric acid gas, leaving 1 volume of hydrogen unabsorbed:

$$K + 2HS = KS, HS + H.$$

Tin heated in this gas forms sulphide of tin, and leaves pure hydrogen gas, of the same volume as the original. (Gay-Lussac & Thénard.)

Combinations. *a*. With Water:—*α*. Hydrate *of Hydrosulphuric acid.* 1. When persulphide of hydrogen enclosed in a sealed tube, and perhaps a little moist, has resolved itself into sulphur and liquid hydrosulphuric acid (II. 197), there are formed, after a time, a few transparent and colourless crystals, which, on opening the tube, immediately liquify, and then disappear with violent evolution of gas.—2. When hydrosulphuric acid gas is passed, at a temperature of —18° (0° F.) through alcohol, which is mixed with such a quantity of water, that the water does not freeze at —18° (or through acetic ether), crystals are produced resembling ice, and apparently of an octohedral form. As soon as the vessel is taken out of the freezing mixture, these crystals disappear with brisk effervescence: enclosed in a sealed tube, they disappear at ordinary temperatures, but

reappear every time the tube is cooled down to — 18°. (Wöhler, *Ann. Pharm.* 33, 125.)

β *Aqueous solution of Hydrosulphuric acid, Hydrosulphuric acid water, Sulphuretted Hydrogen Water.* Water at ordinary temperatures absorbs its own volume of hydrosulphuric acid gas, according to Henry & Dalton; at 18° (0° F.), according to Th. Saussure, 2½ times its volume; and at 11° (52° F.) according to Gay-Lussac & Thénard, 3 times its volume. To prepare this solution, the gas previously washed with water (*App.* 43) is passed alternately through each of two bottles half-filled with water: while it is being passed through one, the other is closed with the stopper and shaken, to ensure complete absorption; and thus the process is continued till the water is completely saturated. One of the bottles is then completely filled with the liquid, and removed with the mouth downwards. —Colourless liquid, having the odour of putrid eggs, sweetish and faint. When heated, it evolves the whole of the gas. Sulphur is precipitated from this liquid by the oxygen of the air, by that of peroxide of hydrogen, sulphurous, selenious, iodic, bromic, hyponitric, and nitric acid, also by iodine, bromine, and chlorine,—the hydrogen of the hydrosulphuric acid combining with the oxygen, iodine, bromine, or chlorine. The air precipitates the sulphur slowly, in the form of milk of sulphur: according to Vauquelin (*J. Pharm.* 11, 126), a small quantity of sulphuric acid may be produced at the same time. Peroxide of hydrogen does not render sulphuretted hydrogen water milky in less than a quarter of an hour. (Thénard.) Sulphurous acid likewise precipitates sulphur slowly: selenious acid produces an immediate precipitate of selenide of sulphur. Iodine in excess produces sulphuric acid, but only when heat is applied; chlorine produces it at ordinary temperatures. Mercury shaken up with sulphuretted hydrogen water does not abstract the whole of the sulphur, even in the course of several months. (O. Henry, *J. Pharm.* 9, 486.) If the liquid be left in contact with air and metal at the same time, the metal quickly abstracts the sulphur, while the hydrogen combines with the oxygen of the air. Sulphuretted hydrogen water kept for three quarters of a year in a bottle containing air was found to contain sulphate of ammonia. (Herzog. *N. Br. Arch.* 3, 167.)

b. With several Salifiable Bases. *Hydrosulphates.* (Vid. *Metallic Sulphides.*)—*c.* With Bisulphide of Carbon.—*d.* With Metallic Sulphides. —*e.* With Cyanogen, Hydrosulphocyanic acid, Alcohol, Volatile and Fixed Oils.

Sulphur and Carbon.

A. Bisulphide of Carbon. CS^2.

Schwefel-kohlenstoff, Schwefel-alcohol, Carbure de soufre, Percarbure de soufre, Soufre carburé liquide, Acide sulfocarbonique of Couerbe;—improperly: *Liquid Sulphuretted Hydrogen, Flüssiger Wasserstoff-schwefel, Soufre hydrogéné liquide.*

Formation. When sulphur is brought in contact with carbon at a red heat; when sulpho-cyanogen is heated; and when wax, sugar, resin, and other organic substances are heated with sulphur. From a mixture of sulphur and charcoal-powder, the sulphur volatilizes before the charcoal has obtained the temperature required to induce combination. (Clement & Desormes.)

Preparation. 1. By passing sulphur vapour over ignited charcoal. The charcoal must be freed as completely as possible from water and hydrogen by ignition, because those substances would convert the first portions of sulphur into hydrosulphuric acid. It is used in small pieces, or in very coarse powder: in the state of fine powder, it would not give free passage to the sulphur.—*a.* A porcelain tube filled with charcoal is connected at one end with a receiver, and at the other with a glass tube containing pieces of sulphur, and closed by a stopper through which a wire passes. As soon as the porcelain tube is red hot and the charcoal has ceased to evolve gas, the pieces of sulphur are gradually pushed, one after the other, into the tube. (Clement & Désormes.)—*b.* A cast-iron tube (water-pipe), 5 feet long and 1¼ inch wide, is filled with charcoal from *b* to *c* (*App.* 46) and surrounded with fire; into the upper end of this, a small iron tube *a* is luted with a mixture of moist clay and a small quantity of iron filings, sulphur, and sal ammoniac. Through this tube the sticks of sulphur are pushed at regular intervals, by means of a rod, into the tube *b*, and the tube *a* is closed with a stopper. Another smaller tube *d* is attached to the lower end of the large tube, and connected by means of the funnel *e* with the tubulated receiver *f*; and this receiver is connected by a bent tube with a well cooled Woulfe's bottle *g*. Since part of the sulphur passes through without combining with the carbon, the neck of the funnel and that of the receiver must be very wide, or they will be stopped up by the sulphur. If the process be long continued, fresh pieces of charcoal must be introduced from time to time through the tube *a*. By this process, two or more pounds of the compound may be obtained in the course of the day. The tube lasts a long time, in fact till it is completely corroded by the formation of sulphide of iron. (Gm.)—*c.* Two black-lead crucibles, each of the capacity of 3 oz., are ground at the edges, to make them fit each other well, and then luted together. (*App.* 48.) The vessel thus formed is filled with pieces of charcoal of the size of half a cubic inch, and placed in an air-furnace having a good draught. A glass tube *a* furnished with a stopper passes through the bottom of the upper crucible, and reaches nearly to the bottom of the lower one. To protect the upper end of the tube, by which the sulphur is introduced, from the heat, the iron plate *k k* is fixed upon the upper crucible, as represented in the figure. A curved earthen tube *c*, an inch wide, is luted into an aperture in the side of the upper crucible near the top, and serves to convey the vapours through the glass tube-funnel *d*, 3 feet long, into the Woulfe's bottle *e*. This bottle contains a little water, which must not, however, exert any pressure. A stick of sulphur an inch long is pushed in every minute [?]; and in two hours, from 12 to 14 ounces of bisulphide of carbon are obtained. (Brunner, *Pogg.* 17, 484.)—*d.* A porcelain tube *a* is luted into the tubulure of a coated earthen retort *b* (*App.* 47), so as to reach within an inch and a half of the bottom. The retort is filled by the neck with pieces of charcoal of the size of hazel-nuts, and placed in the air-furnace in a slightly inclined position, so that the porcelain tube may be a little on one side, and the furnace covered on that side with a tile. The neck of the retort is connected by the bent tube-funnel *c* with the two bottles *d* and *e*. In a few hours, upwards of a pound of sulphide of carbon is obtained. (Pleischl, *Zeitschr. Phys. v. W.* 3, 97.)—*e.* A coated, cylindrical, earthenware bottle *b*, 10 inches wide and 24 inches high, is filled with pieces of charcoal of the size of a cubic inch, and placed directly on the grate of the air-furnace, a fire-space 5 inches wide being left between the bottle and the walls of the furnace. A tube *a*, fitting into

the side of the bottle at its lower part, passes upwards from the furnace in a slanting direction, and through this the sulphur is introduced. Over the upper opening of the bottle is luted an earthenware head *c*, having a long beak, 2 inches wide. By this the vapours are conducted through a refrigerating tube *d*, of iron plate, 4 feet long and 4 inches wide, into the receiver *f*, also made of iron plate. This receiver is surrounded by an outer cylinder *e* filled with ice. From it the sulphide of carbon flows through the tube *h*, fitted into the bottom and dipping into a bottle completely filled with water. The upper opening *g*, which is large enough to admit the hand, is left constantly open, so that the vapour may not escape through the pores of the bottle. For the first two hours, the heat is cautiously applied; but after that, the bottle is kept constantly at a strong red heat. A pound, or a pound and a half of sulphur is introduced through *a* every quarter of an hour. About an hour after the first introduction of the sulphur, the sulphide of carbon begins to come over, and soon flows in a continuous stream. Fifty pounds of sulphur yield, in 12 or 14 hours, from 38 to 40 lbs. of bisulphide of carbon; part of that which is produced is lost by escaping through the pores of the bottle. (Schrötter, *Ann. Pharm.* 39, 297.) This excellent method deserves to be tried with a bottle and head of cast-iron.—*f.* An aperture having been made in the side of a wrought-iron quicksilver bottle, towards the upper part, a curved copper tube is adapted to it, to conduct the vapour into a Woulfe's bottle surrounded with ice; and a straight tube, also of copper, is fitted into the middle opening of the bottle for the purpose of introducing the sulphur. (Mulder, *J. Pharm.* 23, 22; also *J. pr. Chem.* 13, 444.) This form of apparatus is not to be recommended, inasmuch as copper and wrought-iron are quickly corroded by sulphur. Wittstein (*Repert.* 66, 62) obtained only a few ounces of sulphide of carbon from $1\frac{1}{2}$ lb. of sulphur in 7 hours, while the metal of the bottle and tubes was converted into sulphide.

2. Charcoal is heated in an earthenware or porcelain retort fitted with tube-funnel and receiver, in contact with metallic sulphides which give up their sulphur with tolerable facility: *e. g.*, 4 parts of iron or copper pyrites pounded and mixed with 1 part of charcoal; or bituminous wood penetrated with sulphur pyrites. (Lampadius.) Tersulphide of antimony with charcoal requires a strong heat, and yields but a scanty product. (Clement & Désormes.) But 10 parts of tersulphide of antimony with 1 part sulphur and 3 parts charcoal yields—besides $\frac{1}{7}$ pt. brown sulphide of antimony, which collects on the surface of the water in the receiver—a brown distillate, which, when rectified, yields $1\frac{2}{7}$ pt. bisulphide of carbon. The residue in the retort may be mixed with fresh sulphur and charcoal, and used again. (Lampadius, *J. pr. Chem.* 4, 451.)

Purification. Bisulphide of carbon prepared by either of the methods above described contains excess of sulphur in solution, from which it may be freed by distillation in a glass retort over the water-bath. When the distillation is conducted slowly, the residual sulphur forms beautiful crystals. Any water which adheres to the liquid may be removed by distillation from chloride of calcium. Hydrosulphuric acid may be got rid of by agitation with white lead.

Properties. Transparent and colourless; very fluid. Specific gravity 1·300 (Lampadius); 1·272 (Berzelius & Marcet); 1·263 (Cluzel); 1·265 (Couerbe). Of strong refracting power. Does not solidify at —52°. Boiling point, from 40·5° to 45·5° (Berzelius & Marcet); 45° (Couerbe); 46·6° (Gay-Lussac). Tension, density, refractive power, and latent heat

of the vapour (I., 268, 279, 95 and 283.) When this liquid evaporates in the air, and still more in vacuo, rapid absorption of heat takes place. (I., 272.) Odour, unpleasantly aromatic; taste cooling, but at the same time intensely sharp and aromatic. Very inflammable. Insoluble in water.

	Calculation.		Bertholl. Thénard & Vauq.	Berz. & Marc.	Couerbe.
C	6	15·79	14·5	15·17	16·205
2S	32	84·21	85·5	84·83	83·795
CS^2	38	100·00	100·0	100·00	100·000

	Vol.	Sp. gr.
Carbon vapour	1	0·4160
Sulphur vapour	2	2·2185
Vapour of CS^2	1	2·6345

(CS^2 = 76·44 + 2 . 201·17 = 478·78. Berzelius.)

Cluzel thought that he had found in 100 parts of bisulphide of carbon, 28·49 carbon, 58·67 sulphur, 6·98 nitrogen, and 5·86 hydrogen.

Decompositions. 1. Bisulphide of carbon takes fire in the air at 360°, according to Berzelius & Marcet; under 100°, according to Lampadius (*J. pr. Chem.* 4, 391); and burns with a blue—or, according to Vauquelin & Robiquet, with a white and purple red flame. Its combustion in oxygen gas developes heat sufficient to melt platinum wire. (Berzelius & Marcet.) Its vapour mixed with oxygen gas and inflamed in Volta's eudiometer by the electric spark, produces a most violent explosion: a drop of it evaporated in 6 cubic inches of air in the air-pistol, produces, according to Böttger (*J. pr. Chem.* 12, 368), a sharp detonation when inflamed. The products of the combustion are always sulphurous and carbonic acid (*Sch.* 26), or carbonic oxide, if the supply of oxygen is too small to form carbonic acid. (Berzelius & Marcet.) According to Cluzel, water and nitrogen gas are likewise produced.

2. Cold oil of vitriol decomposes bisulphide of carbon into sulphur and carbon, the latter of which blackens the lower stratum of the oil of vitriol. The vapours of these two substances passed simultaneously through a red-hot porcelain tube yield carbonic oxide (no carbonic acid), sulphurous acid, hydrosulphuric acid, and sulphur. (Brault & Poggiale, *J. Pharm.* 21, 137.) Vapour of bisulphide of carbon detonates with hypochlorous acid gas, forming carbonic acid, sulphuric acid, chloride of sulphur, and chlorine; with solution of hypochlorous acid, it yields carbonic, sulphuric, and hydrochloric acid, together with free chlorine. (Balard.)

¶ When vapour of bisulphide of carbon and dry chlorine gas are passed together through a red-hot porcelain tube filled with fragments of porcelain, and thence into a receiver surrounded by a freezing mixture, a yellowish-red liquid is obtained, which is a mixture of chloride of sulphur and perchloride of carbon (C^2Cl^4). When a few grammes of bisulphide of carbon are placed in a vessel of dry chlorine gas, and left for some days or weeks at the ordinary temperature of the air, a dark yellow liquid is produced, consisting of chloride of sulphur, together with a compound of chlorine, sulphur and carbon, whose composition is represented by the formula CSCl: it may be regarded as *Phosgene* (COCl), in which the atom of oxygen is replaced by an atom of sulphur. (Kolbe, *Ann. Pharm.* 45, 41.) ¶

3. When vapour of bisulphide of carbon is passed over ferric, manganic, or stannic oxide kept at a red heat in a glass tube, the products are

a metallic sulphide, together with carbonic and sulphurous acid gas, and without a trace of water. (Berzelius & Marcet.)

$$3SnO^2 + 2CS^2 = 3SnS + 2CO^2 + SO^2.$$

On passing the vapour over ignited baryta, strontia, or lime, there is formed—with ignition in the case of lime—a mixture of 2 atoms of sulphide with 1 of carbonate. (Berzelius, *Sch.* 59.)

$$3BaO + CS^2 = 2BaS + BaO, CO^2.$$

On the other hand, when vapour of bisulphide of carbon is passed over gently ignited carbonate of potassa, carbonic acid is evolved, and there remains a brownish-black fused mixture of 1 atom of tersulphide of potassium and 1 atom of charcoal. (Berzelius, *Sch.* 62.)

$$2(KO, CO^2) + 3CS^2 = 3CO^2 + 2KS^3 + 2C.$$

Possibly, the 2C is at first combined with the $2KS^3$; but on digestion with water, it remains undissolved.

Becquerel's account of the decomposition of nitrate of copper covered with bisulphide of carbon (I., 400) requires, according to Wöhler (*Pogg.* 17, 482), the following corrections: (1.) The black substance is not charcoal, but sulphide of copper, formed from the excess of sulphur dissolved in the sulphide of carbon; hence it is produced without the addition of nitrate of copper. (2.) The copper is quickly converted into non-crystalline sulphide of copper, if the sulphide of carbon is merely covered with very dilute nitric acid.

4. Heated potassium takes fire in vapour of sulphide of carbon, burns with a reddish flame, and becomes covered with a blackish crust. This substance dissolves in water, with separation of charcoal, producing a black carbonaceous liquid. (Berzelius.)—5. Bisulphide of carbon passed in the state of vapour over a quantity of red-hot iron or copper not sufficient to decompose it completely, is converted into a very thin, rose-coloured liquid having a sharp taste. This liquid probably contains monosulphide of carbon (CS), together with undecomposed bisulphide. The copper is converted into sulphide, and, according to Cluzel (Berthollet, Thénard & Vauquelin assert the contrary), covered with a carbonaceous substance.

6. Bisulphide of carbon, kept for a long time under water in vessels containing air, acquires a yellow colour, and is partially converted by oxidation into carbonic and sulphuric acid. (Berzelius.) When water is heated with bisulphide of carbon in a sealed glass tube, the heat being continually increased, it first becomes milky, and afterwards clear, the colour being greenish at the beginning, but gradually becoming darker, and at last nearly black. The bisulphide of carbon rises to the top of the water and then passes to the state of vapour. On cooling, the green colour of the water passes into yellowish, and the bisulphide of carbon again sinks to the bottom. If the water contains chlorate of potassa, it assumes a lemon-yellow colour when heated rather strongly in contact with the sulphide of carbon—effervesces—and deposits a drop of an oily liquid, which disappears on the application of a stronger heat, melted sulphur being separated at the same time. On cooling, the bisulphide of carbon is found to be decomposed, and the chlorate of potassa no longer crystallizes out. When the tube is opened, gas (carbonic acid ?) escapes with a strong explosion, and the water exhibits a strongly acid reaction. (Cagniard de la Tour, *Ann. Chem. Phys.* 23, 267.)

7. Bisulphide of carbon dissolves gradually in aqueous solutions of the fixed alkalis, and forms a brown solution containing an alkaline carbo-

nate and a compound of bisulphide of carbon with a metallic sulphide (Berzelius),

$$3KO + 3CS^2 = KO, CO^2 + 2\,(KS, CS^2)$$

or an alkaline carbonate and an alkaline hydrosulpho carbonate,

$$3KO + 2CS^2 + 2HO = KO, CO^2 + 2\,(KO + HCS^3).$$

8. Bisulphide of carbon placed for a long time in contact with solution of ammonia, forms a dark, brown-red liquid containing hydrosulphocarbonate and hydrosulphocyanate, but no carbonate of ammonia (Zeise, *Schw.* 41, 171), probably in this way:

$$4NH^3 + 4CS^2 = 2(NH^3, HCS^3) + NH^3, HC^2NS^2.$$

9. Bisulphide of carbon dissolves very abundantly in alcohol saturated with ammoniacal gas. The solution remains alkaline, even with a large excess of sulphide of carbon. Even when protected from the air it soon turns yellow, then brown, and smells of hydrosulphuric acid. After the lapse of from 10 to 30 minutes, it deposits yellow feathery crystals of hydrosulphocarbonate of ammonia; then more shining crystals of hydrosulphocyanate of ammonia are formed, while those of the hydrosulphocarbonate diminish in quantity. The alcoholic liquid still retains very large quantities of hydrosulphocyanate and hydrosulphate of ammonia, which, on distillation or exposure to the air, are resolved into hydrosulphate of ammonia, which escapes, sulphur which crystallizes out, and sulphocyanate of ammonia which remains in solution. (Zeise.) In the first instance, probably, 3 atoms of ammonia and 3 atoms of bisulphide of carbon resolve themselves into 1 atom of hydrosulphocarbonate and 1 atom of hydrosulphocyanate of ammonia:

$$3NH^3 + 3CS^2 = NH^3, HCS^3 + NH^3, HC^2NS^2, HS.$$

The subsequent diminution of the hydrosulphocarbonate and increase of the hydrosulphocyanate, with formation of hydrosulphate of ammonia probably arises from the resolution of 2 atoms of hydrosulphocarbonic acid and 1 atom of ammonia into 3 atoms of hydrosulphuric acid and 1 atom of hydrosulphocyanic acid. (Zeise.)

$$NH^3 + 2HCS^3 = 3HS + HC^2NS^2, HS.$$

[For the formation of xanthonate of potassa from bisulphide of carbon, potash, and alcohol, vid. *Xanthonic acid.*]

Combinations. *a.* Miscible in all proportions with liquid carbonic acid.—*b.* With phosphorus.—*c.* With sulphur.—*d.* With hydrosulphuric acid.—*e.* With iodine.—*f.* With bromine.—*g.* With chloride of sulphur.—*h.* With chloride of nitrogen.—*i.* With ammonia.—*k.* With metals, *e. g.* copper?—*l.* With metallic sulphides. (*q. v.*).—*m.* With alcohol, ether, volatile and fixed oils, camphor, and resins.

B. Sulphuretted Bisulphide of Carbon.—Bisulphide of carbon may be made to combine, by solution, with an additional quantity of sulphur, whereby it acquires a yellowish colour. When the liquid is distilled, or when it evaporates or burns in the air, this excess of sulphur remains behind; it likewise crystallizes very beautifully from a solution formed at a higher temperature. The excess of sulphur is likewise precipitated on mixing the liquid with ether, alcohol, or a hot solution of caustic potash. Amalgam of lead or silver agitated with it also removes the sulphur, forming sulphide of lead or sulphide of silver. (Berzelius.)

C. Sulphuretted Charcoal.—Charcoal which has been used in the preparation of bisulphide of carbon (method 1) contains a quantity of sulphur so intimately united, that it cannot be removed by ignition: sulphate of potassa is however obtained when the charcoal is deflagrated with nitre. (Clement & Désormes.) The same substance is obtained by washing gunpowder with water to remove the nitre, and then heating it strongly to drive off sulphur. (Proust.) According to Berzelius, this compound should be regarded as a *Supercarburet of Sulphur*.

D. Hydrosulpho-carbonic Acid. HCS^3.

Red Acid, Rothsäure, Säure des rothwerdenden Salzes, Hydrothio-carbonsäure (Zeise); *Kohlenschwefelwasserstoffsäure.* (Berzelius.)

Formation. 1. (II. 204, 7.) 2. Aqueous solutions of alkaline hydrosulphates or monosulphides of the alkali-metals rapidly dissolve bisulphide of carbon, forming a brown solution of an alkaline hydrosulphocarbonate, or of a compound of bisulphide of carbon with a metallic sulphide. (Berzelius.)

Preparation. Hydrosulphocarbonate of ammonia, dried and pressed, is put into slightly diluted hydrochloric acid; more water is then quickly added, and the supernatant watery liquid decanted off from the oily acid as it settles down. If the quantity of hydrochloric acid is too great, the oily matter redissolves, and if the hydrochloric acid is too concentrated, sulphuretted hydrogen is evolved. (Zeise.)

Properties. Red-brown, transparent, oily liquid, heavier than water; has an odour like that of hydrosulphuric acid, but at the same time characteristic. Gives a red precipitate with lead salts, red-brown with cupric, salts and yellowish with mercuric salts. All these precipitates turn black in a few hours. (Zeise.)

Zeise's Calculation.			Or:		
H	1	1·82	CS^2	38	69·09
C	6	10·91	HS	17	30·91
3S	48	87·27			
HCS^3	55	100·00	CS^2, HS	55	100·00

(CS^2 + HS = 478·78 + 213·65 = 692·43. Berzelius.)

Combinations. *a.* This acid dissolves in aqueous hydrochloric or sulphuric acid.

b. It combines with salifiable bases, forming salts called *Hydrosulphocarbonates* (vid. *Metallic Sulphides*).

Sulphur and Boron.

A. Sulphide of Boron.—Boron heated to redness in sulphur vapour takes fire and burns, producing sulphide of boron, which forms a white, opaque deposit on the sides of the vessel, but appears grey at the bottom, from being mixed with uncombined boron. Sulphide of boron decomposes water with violence, sulphuretted hydrogen being evolved, and boracic

acid remaining in solution. On treating the grey sulphide of boron above mentioned with water, the pure boron mixed with it falls to the bottom. If the boron be merely heated in the sulphur vapour till it takes fire, and no stronger heat be afterwards applied, a sulphide of boron containing excess of sulphur is formed; and this, when digested in water, deposits the excess of sulphur in the form of milk of sulphur. (Berzelius, *Pogg.* 2, 145.) When sulphur is melted with boron, an olive-coloured mixture is obtained, from which, according to Berzelius, the sulphur may be separated by distillation.

B. Sulphate of Boron? Boron dissolves in hot oil of vitriol with slight effervescence, forming a black liquid, which gives a black precipitate with potash. (H. Davy.)

C. Sulphate of Boracic Acid. Boracic acid, whether anhydrous or crystallized, dissolves in oil of vitriol in large quantity, especially at an elevated temperature, forming a colourless compound of the consistence of turpentine: part of the boracic acid separates from it spontaneously. (Gm.)

Sulphur and Phosphorus.

A. Sulphides of Phosphorus.

Sulphur and phosphorus unite in all proportions, and with vivid combustion and powerful detonation. Small quantities of phosphorus and sulphur, both in a state of dryness, heated together in a glass tube, enter into combination, and evolve so much heat, that the compound is rapidly converted into vapour, and the tube bursts with a loud report. Explosion also takes place, according to Pelletier, when the sulphur and phosphorus are melted together under water, especially if the heat be too suddenly applied, and the two bodies are about equal in quantity.

1. Sulphur is added in successive portions to phosphorus kept in a fused state under water (Pelletier); or the two bodies are rubbed together under warm water. (Levol.)—2. The two substances are melted together under boiling alcohol of 80 per cent. (R. Böttger.)—3. Or under alcoholic solution of potash. (R. Böttger.)—4. Under heated rock-oil. The combination takes place without explosion, even with large quantities; and the rock-oil is not decomposed, merely dissolving a little of the compound; whereas, oil of turpentine is decomposed, and acquires an intolerably bad odour.—5. Phosphorus is heated in an alcoholic solution of potash liver of sulphur, the liquid being agitated, and then left to stand for some days. The best method is however as follows: An alcoholic solution of potash is saturated at a boiling heat with flowers of sulphur; phosphorus is heated to fusion in the dark-red filtrate, the liquid being carefully agitated; the flask is left open for several days in a dark place, and the whole frequently warmed and shaken up; then after cooling, the liquid sulphide of phosphorus is several times washed with water in the dark—agitated, while still a little turbid, with ether—and kept under ether in a dark place. Sulphide of phosphorus obtained by this method is a transparent liquid, whereas that obtained by other methods is mixed with crystals of sulphur. (R. Böttger.)—6. By decomposing terchloride of phosphorus with hydrosulphuric acid, pale yellow tersulphide of phosphorus is obtained. (Serullas.)

$$3HS + PCl^3 = 3HCl + PS^3.$$

Turbid sulphide of phosphorus may be rendered transparent by agitation with aqueous ammonia (Faraday), or by pressure through chamois leather. (Böck, Dupré.)

Pale yellow; friable and semitransparent when in the solid state—oily and transparent when liquid. Phosphorus crystallizes out from mixtures containing excess of phosphorus; and sulphur from those which contain excess of sulphur. (Faraday, Mitcherlich, Böttger.) According to Dupré, that which crystallizes out is not sulphur, but sulphide of phosphorus with six atoms of sulphur.

P^4S (8 pts. to 1 pt.) solidifies at + 25°.—P^2S (4 pts. to 1 pt.) solidifies at 15° (Pelletier).

PS (2 pts. to 1 pt.) solidifies at + 10° (Pelletier), at + 4° (Faraday); according to Dupré, it does not solidify till kept for a long time at — 19°, and afterwards melts at + 5° or + 6°; sp. gr. 1·80.

The compound of 7 pts. phosphorus with 5 pts. sulphur is at first liquid even at — 6·7°, but subsequently deposits crystals of sulphur, whilst PS, which solidifies at + 4°, remains. (Faraday.)

PS^2 (1 pt. to 1 pt.) solidifies at + 5° (Pelletier), melts at 11·25° Böttger); remains liquid at — 4°, but PS^6 crystallizes out. (Dupré.)

PS^3 (2 pts. to 3 pts.) remains liquid at — 4°, but contains crystals of PS^6. (Dupré.)

PS^4 (1 pt. to 2 pts.) solidifies at + 12·5°, but is resolved at the same time into a crystalline and a liquid part. (Pelletier.)

PS^6 (1 pt. to 3 pts.) solidifies at 37·5°, forming a friable mass. Melts in boiling water; solidifies on cooling to a transparent, lemon-yellow, crystalline-grained, and tolerably solid mass, which becomes doughy when rubbed at a temperature of 15°. Crystallizes on cooling from PS^2, and still better from PS^3, in pale-yellow transparent crystals, which must be dried between bibulous paper frequently renewed. Specific gravity 2·02; begins to melt at 100°, and solidifies to a crystalline mass on cooling. (Dupré.)

Sulphide of phosphorus kept under ether quickly loses its transparency in diffused daylight, and still more quickly in direct sunshine, becoming covered with a white film, which, however, disappears again if the substance be kept in the dark: it does not assume a red colour, either in ether or in water, as Böckmann formerly observed, or yet in alcohol. (Böttger.) Sulphide of phosphorus fumes and shines in the air; with that which consists of equal parts of the two elements, this effect takes place at — 1°. (Heinrich.) PS fumes less in the air than phosphorus, but takes fire more easily: PS^6 fumes and shines less, and does not take fire till heated above 100°; when rapid combustion takes place, sulphurous and phosphoric acids are produced. (Dupré.)—Nitric acid of 1·52 specific gravity placed in contact with sulphide of phosphorus evolves nitrous acid fumes attended with violent hissing, and sets fire to the substance in a few minutes; nitric acid of 1·2 sp. gr. and likewise oil of vitriol or hydrochloric acid, does not act sensibly on it at ordinary temperatures. (Böttger.) With solution of hypochlorous acid, sulphide of phosphorus yields sulphuric, phosphoric, and hydrochloric acids, and chlorine. (Balard.) Sprinkled upon iodine at 14°, it instantly takes fire, and burns with a large and tolerably quiet flame. (Böttger.) Sulphide of phosphorus kept under water swells up by degrees; evolves hydrosulphuric acid gas, which is luminous in the dark, from the presence of vapour of sulphide of phosphorus; and imparts an acid of phosphorus to the water

(Pelletier.) Tersulphide of phosphorus gradually disappears under water, with formation of hydrosulphuric and phosphoric [phosphorous] acids (Serullas, *Ann. Chim. Phys.* 42, 33.) A mixture of one part phosphorus and three parts sulphur does not act upon water, except in sunshine: the action is quicker between 80° and 100°; the water becomes turbid and impregnated with hydrosulphuric acid. Part of the hydrosulphuric acid produced appears to remain combined with sulphur in the form of persulphide of hydrogen, which mixes with the sulphide of phosphorus, and renders it more fusible. This explains the diversity in the statements respecting the melting point; and the subsequent decomposition of the persulphide of hydrogen accounts for the swelling up of the sulphide of phosphorus. Solid sulphide of phosphorus also becomes liquid on the addition of persulphide of hydrogen; it likwise softens when a stream of hydrosulphuric gas is directed upon it under water: ammonia instantly makes it solid again, and at the same time acquires a yellow colour. (Levol.) Bisulphide of carbon in which an equal weight of sulphide of phosphorus is immersed, extracts the phosphorus first, and separates the greater part of the sulphur in combination with a small quantity of phosphorus. Strong boiling solution of potash extracts the sulphur from the compound, leaving colourless and transparent phosphorus; the latter, however, again takes up the sulphur from the liquid, when left in contact with it for some time. (Böttger.) Sulphide of phosphorus readily combines with fixed oils, producing phosphorescent mixtures.

¶ The sulphides of phosphorus have, within the last few years, been more particularly examined by Berzelius,—from whose investigations it appears that phosphorus forms with sulphur a series of compounds precisely analogous in composition to those which it forms with oxygen; that is to say, to phosphoric oxide, hypophosphorous acid, phosphorous acid, and phosphoric acid. Moreover, some of these compounds may be obtained in two isomeric conditions, in one of which the phosphorus appears to exist in its ordinary state, in the other, in its red modification, or the state into which it is brought by the action of light or heat. (*Vid.* p. 108.)

I. Disulphide of Phosphorus. P^2S.

Hypo-sulphophosphorous acid, Phosphorous Hyposulphide, Hyposulfide phosphoreux, Phosphorsulfuret.

a. Ordinary Modification. Prepared by fusing together a mixture of sulphur and phosphorus in the proportion of two atoms of phosphorus to one atom of sulphur. The materials may be fused under boiling water—or else in a tube in which they have been weighed—the tube being first sealed with the blow-pipe, and then left to itself till all the oxygen of the air which it contains has combined with the phosphorus. The quantity of phosphorus consumed by this oxidation is too small to exert any appreciable influence on the result. The temperature to which the materials are subjected should not exceed 100°; hence the fusion is best performed by the heat of a water-bath. The sulphur combines with the phosphorus at the moment when the latter melts.—2. By digesting phosphorus in an alcoholic solution of persulphide of potassium (liver of sulphur). The phosphorus reduces the persulphide, to a lower degree of sulphuration, and is itself converted into disulphide of phosphorus without taking an additional portion of sulphur from the excess of alkaline persulphide.

Properties. At and above 0°, the disulphide of phosphorus is a transparent, colourless liquid, having the consistence of a fixed oil. At a somewhat lower temperature it solidifies, forming a mass of slender, colourless crystals. Fumes in the air, and exhales the odour of phosphorus. In an atmosphere free from oxygen, it may be distilled without alteration. Readily takes fire in the air, particularly when absorbed by porous bodies. Insoluble in alcohol and ether; but these liquids are gradually altered by it, even out of contact of air; and the new products dissolve in the liquid, while the remaining sulphide undergoes no alteration, but merely diminishes in volume. Oils, both fixed and volatile, dissolve it in small quantity: the solution shines in the dark, and gives off slight fumes when in contact with the air.

The composition of disulphide of phosphorus is :—

	Calculation.		Berzelius.
2P	62·8	79·69	79·592
S	16·0	20·31	20·408
P^2S	78·8	100·00	100·000

(P^4S = 4 . 196·14 + 201·17 = 985·73. Berzelius.)

Decompositions. 1. This compound may be preserved without alteration in a bottle filled with boiled water and well corked; but in water impregnated with air, the phosphorus gradually oxidizes at the expense of the air, and is converted into phosphoric acid; hence the liquid acquires an acid reaction. When boiled with water, it slowly exhales hydrosulphuric acid.—2. When it is digested in solution of potash or soda, the phosphorus is converted into phosphoric acid, by taking oxygen both from the alkali and from the water,—while the alkali-metal and the hydrogen of the water combine with the sulphur. The products are therefore an alkaline phosphate, an alkaline hydrosulphate, and a polysulphide of the alkali-metal; and there finally remains a quantity of phosphorus free from sulphur, which solidifies on cooling.

Disulphide of phosphorus dissolves, with the aid of heat, an additional quantity of phosphorus; but deposits it again in the form of rhomboidal dodecahedrons on cooling.

b. Red Modification. Formed when the preceding substance, or the liquid protosulphide of phosphorus next to be described (p. 212), is gently heated in contact with an electro-positive metallic sulphide. It is best prepared as follows :—A layer of anhydrous carbonate of soda two inches thick is placed in a tube six or eight inches long, and a quantity of liquid protosulphide of phosphorus poured upon it, drop by drop, till the carbonate of soda is slightly impregnated with the liquid throughout. The tube is then closed with a cork, through which a gas-delivery tube passes, and immersed in a sand-bath, to such a depth that the level of the sand may be a little above that of the salt within the tube. The sand-bath is raised to a temperature sufficient to maintain the water in a vessel placed beside the tube in a state of constant ebullition. On withdrawing the tube from the sand from time to time, it is found that the mass first turns yellow without fusing, and afterwards assumes a red colour, which commences at the bottom, and gradually extends itself upwards, increasing at the same time in intensity. Above the saline mass there is deposited, on the sides of the tube, a spontaneously inflammable sublimate of phosphorous acid, formed at the expense of the air already contained in the tube, and of that which enters slowly and insensibly through the gas-delivery tube.

As soon as the red colour ceases to spread any further, the tube is withdrawn from the sand-bath and left to cool. When it is perfectly cold, it must be scratched with a file, a line or two below the upper limit of the red tint, then broken at that point, and the two ends immediately thrown into separate vessels of water; the surfaces of the saline mass would take fire instantly on coming in contact with the air. The water dissolves out a quantity of sulphophosphite of sodium and of phosphate and carbonate of soda, while a red powder is left behind. This is to be well washed with cold water, previously freed from air by boiling, and then left to dry on the filter placed upon blotting-paper to absorb the moisture. If it were dried in vacuo over sulphuric acid, it would take fire as soon as the air was readmitted; and if it were dried in the air over sulphuric acid, it might also take fire when withdrawn from under the bell-jar, in consequence of the heat produced by the rapid condensation of the aqueous vapour. If it contains the minutest portion of liquid protosulphide of phosphorus, it is sure to take fire during the process of drying. The powder obtained by this process is the red disulphide of phosphorus. By the action of heat on the mixture of carbonate of soda and protosulphide of phosphorus, sulphophosphite of soda and disulphide of phosphorus are formed. If the quantity of protosulphide is too small, phosphorus is set free; and when it is too great, other red compounds are produced containing less phosphorus. It is essential therefore that the protosulphide be not added in excess. The phosphorous acid deposited above the saline mass is chiefly produced from phosphorus which cannot find sufficient sulphur to combine with: this portion of phosphorus sublimes at a temperature at which the red disulphide is fixed. If the temperature rises during the preparation (which however can hardly happen with an ordinary sand-bath), the mass blackens without fusing; the phosphorus reduces the carbonic acid, and a quantity of charcoal is obtained impregnated with phosphorus and mixed with phosphate and metaphosphate of soda, besides persulphide of sodium.

Properties. Red disulphide of phosphorus is of a beautiful, deep, vermilion-colour, much like that of phosphoric oxide prepared in the dry way, but purer. It is always in the state of powder; and when examined by the microscope, exhibits brilliant angular surfaces, indicative of a crystalline structure; but the smallest grains of it are opaque. It has neither taste nor smell. Heated in a small distillatory apparatus filled with hydrogen gas, it volatilizes without fusing. At the same time, its colour becomes less intense, and ultimately black or black-brown; but on cooling, it regains its original colour. During the application of the heat, it continually diminishes in bulk, and a colourless liquid, which is the liquid disulphide of phosphorus, condenses in the receiver. Hence it appears that this substance, in assuming the gaseous state, passes from the red to the ordinary modification; but this change does not take place till the temperature is raised above the boiling point of the latter. Pure nitric acid of density 1·22 has no action on this compound at first; but, after a certain time, it dissolves suddenly and with great violence. By less concentrated nitric acid, it is not attacked without the aid of heat.

Red disulphide of phosphorus combines with sulphur-bases, imitating in this respect the behaviour of phosphoric oxide with oxygen-bases. In the resulting compounds, the disulphide and the sulphur-base contain equal quantities of sulphur. The compounds are called *Hyposulphophosphites*.

II. Protosulphide of Phosphorus. PS.

Hypo-sulphophosphoric acid, Phosphoric Hyposulphide, Hyposulphide phosphorique, Unterphosphoriges Sulfid.

a. *Ordinary Modification. Preparation.* By fusing together one atom of sulphur and one atom of phosphorus, in the same manner as in the preparation of the disulphide. The compound is apt to become turbid, from the formation of phosphoric oxide at the expense of the oxygen of the air. This oxide first forms on the surface of the liquid, but afterwards sinks into it and remains for a long time in suspension, the liquid ultimately becoming clear. The best mode of clearing it is to collect it in water, making it run into that liquid from a glass tube drawn out at the end, and under the pressure of a high column of water. Another method is to wrap a piece of linen round the end of a glass tube,—pour the sulphide of phosphorus into the tube—then pour a quantity of water on the top of it, and force the liquid through the linen by means of a piston. The clarification may also be effected by agitation with ammonia; but this occasions partial decomposition.

Properties. Transparent, yellow liquid, not very mobile; refracts light strongly. Odour, strong and repulsive, recalling that of phosphorous acid and of chloride of sulphur at the same time. The odour of phosphorous acid arises from the formation of that acid when the liquid comes in contact with the air. Protosulphide of phosphorus may be distilled without alteration in an atmosphere free from oxygen. It is colourless in the gaseous state. At a certain number of degrees below 0°, it solidifies and forms a colourless mass of small interlaced crystals; but its crystallizing point is lower than that of the disulphide. It fumes in the air and is luminous in the dark; likewise emits light when vaporized in nitrogen or hydrogen gas freed from oxygen. It adheres strongly to dry solid bodies: if a small quantity of it gets attached to the fingers, it cannot be removed by water, even with the aid of soap, unless the skin be previously rubbed with oil. Takes fire easily in the air at a slightly elevated temperature, burning with a bright flame, like that of phosphorus, and emitting a thick smoke. It does not take fire spontaneously when a drop of it is let fall on a solid body; but when absorbed by a porous body and exposed to the air, it soon becomes heated and takes fire.

	Calculation.		Berzelius.
P	31·4	66·24	66·192
S	16·0	33·76	33·808
PS	47·4	100·00	100·000

(P^2S = 2 . 196·14 + 201·17 = 593·45. Berzelius.)

Decompositions. 1. When protosulphide of phosphorus evaporates slowly in a confined space (as a bell-jar) filled with moist air, which is slowly but continually renewed, it is converted by oxidation into sulphuric and phosphoric acids, which are deposited in the form of aqueous solution on the sides of the vessel and around the liquid itself.—2. In a limited atmosphere of dry air slowly and continually renewed (as in a glass tube imperfectly closed by a cork) it is gradually converted, in the course of three weeks, into phosphorous acid, which forms a white mass in the upper part of the tube, and takes fire on removing the cork; persulphide of phosphorus (p. 218), which crystallizes at the bottom of the liquid; and

a brown substance, which collects on the sides of the tube, in a layer of continually increasing thickness,—and is resolved by digestion in water for half an hour, into phosphoric and sulphuric acids, and hydrated phosphoric oxide.—3. Placed in a tube imperfectly closed by a cork, and heated in a sand-bath, it is converted into a white, spontaneously inflammable mass, consisting, for the most part, of phosphorous acid.—4. Water has but very little action on this liquid. If it be kept for a few days in a closed vessel filled with boiled water, no visible change takes place; but on opening the vessel, the odour of sulphuretted hydrogen is emitted. When it is kept under water impregnated with air in an open vessel, sulphur is deposited, and renders the water turbid; but the action is so slow, that the sulphide suffers no perceptible diminution, even in the course of several months.—5. With alcohol, ether, and oils, both fixed and volatile, it behaves like the disulphide.—6. It is decomposed by digestion with caustic alkalis, the products being an alkaline phosphate and hydrosulphate, and a polysulphide of the alkali-metal, all of which dissolve in the liquid, so that nothing remains but a small quantity of phosphorus free from sulphur.—7. When it is heated gently in contact with a metallic sulphide in an atmosphere free from oxygen, great heat is evolved, and a considerable portion of the liquid distils over with almost explosive violence: at the same time, a hyposulphophosphate of the metal is produced, in which the sulphide of phosphorus exists in a peculiar isomeric state.—8. On digesting this compound with metallic solutions, sulphides of the metals containing variable quantities of hyposulphophosphate are slowly deposited. The variation in the results arises from oxidation of the phosphorus at the expense of the metallic solution, the quantity thus oxidized depending upon the temperature and the concentration of the solution. The salts thus formed contain sulphide of phosphorus in a different isomeric condition from that obtained in the dry way. From solutions of easily reducible metals, such as silver, nothing but a sulphide of the metal is precipitated. Copper gives a precipitate of hyposulphophosphate. With ammoniacal solution of dichloride of copper, a dark-red precipitate is obtained, resembling suboxide of copper. Sulphate of copper mixed with a sufficient quantity of ammonia to form a blue liquid gives, with protosulphide of phosphorus, a dark-brown precipitate. Both these precipitates are hyposulphophosphates of copper; but the former is of a minimum, the latter of a maximum degree of sulphuration. When these salts are exposed to the air, they become acid from oxidation of the phosphorus. They should therefore, after washing, be rapidly pressed between folds of bibulous paper, and then dried in vacuo over sulphuric acid.

Combinations.—*a.* With Disulphide of Phosphorus.—*b.* With sulphur-bases, forming salts called *Hyposulphophosphates*, which are the analogues of the hypophosphites: its capacity of saturation is such that the sulphur-acid and sulphur-base in these salts contain equal quantities of sulphur. —*c.* With oils, both fixed and volatile.

b. *Red Modification.* Obtained by decomposing hyposulphophosphate of manganese by hydrochloric acid. Protosulphide of manganese, prepared by precipitating a proto-salt of manganese by hydrosulphate of ammonia, washing the precipitate, drying, and gently heating it in a current of hydrosulphuric acid gas, is introduced into the middle bulb of a tube having three bulbs blown upon it, and a quantity of liquid protosul-

phide of phosphorus, sufficient to moisten it thoroughly, poured upon it by means of a pipette. Hydrogen gas previously dried by chloride of calcium is then passed through the tube, so as to drive out the air as quickly as possible, and the middle bulb gently heated by a spirit-lamp. Under these circumstances, the sulphide of phosphorus combines with the sulphide of manganese; and so much heat is evolved, that the excess of sulphide of phosphorus is driven with violence from the middle bulb into the other two. It is afterwards transferred in the direction of the current of hydrogen gas, from the bulb nearest to the chloride of calcium tube into the middle bulb, and lastly into the further one. When it has been completely expelled from the first two bulbs, the apparatus is left to cool, the current of hydrogen gas being passed through it all the time. The heat applied in this process must be very gentle: a spirit-lamp having its wick raised just enough to give a pale blue flame should be held about two inches from the bulb; and even this is sometimes too strong. The colour of the required compound is yellowish green; but if the temperature rises too high, the darker green colour of protosulphide of manganese appears at the lower part of the bulb. When this happens, the apparatus must be allowed to cool, so that the sulphide of phosphorus may be reabsorbed, and the bulb again very gently heated. The yellowish-green substance obtained when the process is properly conducted is the hyposulphophosphate of manganese, MnS, PS. On digesting it in hydrochloric acid, the manganese is dissolved in the form of chloride—hydrosulphuric acid is evolved—and an orange-coloured powder is left, which is a protosulphide of phosphorus.

$$MnS, PS + HCl = MnCl + HS + PS.$$

Properties. Orange-coloured powder, inclining to yellow, closely resembling phosphoric oxide prepared in the wet way. Tasteless and inodorous. Inalterable both in air and water. By dry distillation, it is converted into the liquid protosulphide, without previous fusion. Assumes a darker colour when heated, but regains its original tint on cooling. Takes fire in the air at a temperature near 100°, and burns with a very bright flame, emitting a thick smoke.

Decompositions. 1. When this compound is digested in excess of strong caustic potash at ordinary temperatures, phosphuretted hydrogen gas of the less inflammable variety is disengaged, and the alkali dissolves small quantities of phosphoric acid and tersulphide of phosphorus. On the application of heat, the whole is dissolved, yielding the same products as the liquid modification (p. 213).—2. Caustic ammonia dissolves it, but not without great difficulty. The solution has a strong yellow colour, and yields on spontaneous evaporation, a soft, yellow, semi-transparent mass, which, when treated with water, leaves a small quantity of protosulphide of phosphorus, of a deep yellow colour and pulverulent consistence; whilst another portion dissolves, and may be precipitated by an acid. In this case, a small quantity of hypophosphite of ammonia is formed, together with a substance but slightly soluble in water. This latter substance is composed of sulphide of ammonium and protosulphide of phosphorus, probably with an excess of the latter, which dissolves on washing the undissolved matter, and leaves a slight residue of protosulphide of phosphorus containing ammonia. Acids precipitate the protosulphide of phosphorus from these solutions in the form of yellow flakes, which have a deeper colour in the cold than when heated.

Combination. With red disulphide of phosphorus.—*Preparation.* Sulphide of zinc is prepared by precipitating a zinc-salt with hydrosulphate of ammonia, and afterwards treated with liquid protosulphide of phosphorus, as in the preparation of hyposulphophosphate of manganese. It is sufficient, however, to use a tube with two bulbs, inasmuch as the heat developed is not so great as in the former case. The sulphide of zinc is first converted into yellow hyposulphophosphate of zinc; but afterwards, when the heat is continued till all the liquid protosulphide of phosphorus condensed in the first bulb is driven over into the second, it is converted into a compound of 1 atom of hyposulphophosphate with 1 atom of sulphide of zinc, saturated with 1 atom of disulphide of phosphorus. This compound is of a fine red colour throughout, and yields a powder resembling red lead in external appearance. A liquid distils over containing less phosphorus than the protosulphide, and depositing crystals which have not been examined, but probably consist of pentasulphide of phosphorus. When the red compound just mentioned is treated with strong hydrochloric acid, the sulphide of zinc contained in it is dissolved, with disengagement of hydrosulphuric acid, and there remains a red mass, which, after washing, may be dried either over sulphuric acid or by simple exposure to the air.

This substance is a compound of protosulphide and disulphide of phosphorus.

	Calculation.		Berzelius.	Or:	By Calculation.	
3P	94·2	74·96	74·52	P^2S	78·8	62·44
2S	32·0	25·04	25·48	PS	47·4	37·56
P^3S^2	126·2	100·00	100·00	$P^2S + PS$	126·2	100·00

($P^4S + P^2S = 985{\cdot}73 + 593{\cdot}45 = 1579{\cdot}18$. Berzelius.)

It is of a bright-red colour, like red lead. Has neither taste nor smell, and is unalterable in the air. When submitted to dry distillation, it is converted into a liquid of the same composition: hence, it contains the red modification of phosphorus. Takes fire above 100°, burning with a bright flame, and diffusing a thick smoke. Dissolves in boiling liquid protosulphide of phosphorus, forming a red solution; and when the liquid is distilled off, the compound remains in the form of a dark-red cake, rather soft, and capable of being scratched by the nail.

III. Tersulphide of Phosphorus. PS^3.

Sulphophosphorous acid, Phosphorous Sulphide, Sulfide phosphoreux, Phosphoriges Sulfid.

Discovered by Serullas, who obtained it by the action of hydrosulphuric acid on terchloride of phosphorus, but did not further examine it. (*vid.* p. 207).

Other modes of preparation. 1. Red protosulphide of phosphorus is mixed with the quantity of sulphur required to convert it into the tersulphide (1 atom of PS to 2 atoms of S), and the mixture heated in a small retort. The heat evolved at the moment of combination is so great, that a small portion of the mass is volatilized with violence. The whole then fuses uniformly, and ultimately sublimes in the form of a transparent crystalline substance of a pale lemon-yellow colour. If the distillation be

interrupted before the whole is volatilized, the unsublimed portion retains a reddish colour while hot, but on cooling acquires the same colour as the sublimed portion. The vapour is but slightly coloured.—2. One atom of hyposulphophosphate of manganese is intimately mixed with 2 atoms of sulphur, and the mixture heated in a small retort in an atmosphere free from oxygen, till nothing but protosulphide of manganese remains. Tersulphide of phosphorus is then obtained in the form of a sublimate. If a hyposulphophosphate be employed, the base of which does not so readily give up its sulphur-acid—hyposulphophosphate of silver for example—only half of the tersulphide of phosphorus sublimes, while the rest remains in combination, in the form of sulphophosphite of silver. The principle of this reaction is, that one atom of the sulphur-base is saturated by one atom of protosulphide of phosphorus, whereas one atom of tersulphide of phosphorus requires 2 atoms of a sulphur-base to saturate it: consequently, 2 atoms of hyposulphophosphate produce 1 atom of sulphophosphite and 1 atom of tersulphide of phosphorus:

$$2(MS, PS) + 4S = 2MS, PS^3 + PS^3.$$

Properties. This compound is a solid substance, of a pale yellow colour. After fusion or sublimation, it remains soft, like plastic sulphur, and does not become opaque till it hardens. Sublimes at a temperature below the subliming point of sulphur. When heated in the air, it burns with a whitish-yellow flame, and diffuses a thick smoke. In moist air, it decomposes rapidly, becoming white and assuming an acid reaction, in consequence of the formation of phosphoric acid: at the same time, it acquires a bitter and hepatic taste. This decomposition in the air takes place so rapidly, that the substance can only be preserved in vessels hermetically sealed. The unsublimed reddish tersulphide decomposes in the same way.

Tersulphide of phosphorus is rapidly dissolved by caustic alkalis and by ammonia. The solutions have a pale yellow colour, and when treated with acids, yield a light, flocculent, and nearly white precipitate, which falls down slowly, and has a pale yellow colour when collected in a mass: this precipitate may be washed and dried. Tersulphide of phosphorus in this state is less rapidly decomposed by exposure to the air than that which has been fused or sublimed. It is uncertain whether the difference thus produced by the influence of an alkali depends upon an isomeric modification. Tersulphide of phosphorus is easily dissolved in the cold by carbonate of potassa or soda; but deposits sulphur at the same time—a proof that decomposition takes place.

	Calculation.		Berzelius.
P	31·4	39·55	39·394
3S	48·0	60·45	60·606
PS^3	79·4	100·00	100·000

(P^2S^3 = 2 . 196·14 + 3 . 201·17 = 995·79. Berzelius.)

Combinations. Tersulphide of phosphorus, or *Sulphophosphorous acid* combines with sulphur-bases, forming a class of sulphur-salts called *Sulphophosphites*, which are the analogues of the phosphites. One atom of the sulphur-acid is saturated by 2 atoms of a sulphur-base, just as one atom of phosphorous acid is saturated by 2 atoms of an oxygen-base.

IV. Pentasulphide of Phosphorus. PS^5.

Sulphophosphoric acid, Phosphoric Sulphide, Sulfide phosphorique, Phosphorsulfid.

This compound is formed when sulphur and phosphorus combine with explosion and development of light, being deposited in the form of a light, transparent, pale-yellow film on the bodies on which it cools. This mode of formation is not, however, practically useful.

Preparation. 1. One atom of solid protosulphide of phosphorus is mixed with 4 atoms of sulphur, and the mixture heated in an atmosphere free from oxygen, till the two substances unite. The act of combination is attended with a sudden disengagement of heat, by which a portion of the substance is rapidly sublimed; but there is no explosion or production of light.—2. One atom of hyposulphophosphate of manganese is heated with 4 atoms of sulphur: the required compound sublimes at a gentle heat, leaving protosulphide of manganese. Hyposulphophosphate of silver heated with 4 atoms of sulphur yields sulphophosphate of silver, while half of the pentasulphide of phosphorus sublimes.

Pentasulphide of phosphorus is likewise formed, when the liquid protosulphide is heated in a current of hydrosulphuric acid gas. A pale liquid distils over, which is a solution of the pentasulphide in the liquid protosulphide, and yields a small quantity of the former in crystalline scales.

Properties. This compound is of a pale-yellow colour, like the tersulphide—but crystallizes. When it is sublimed very slowly, and in such a manner that it can form isolated crystals, these crystals are transparent, and have so little yellow colour, that they appear perfectly colourless when thin: their faces are deeply striated. When the liquid pentasulphide is distilled, it assumes a crystalline form in solidifying, and is then easily detached from the glass. When solidified by sudden cooling, it does not crystallize, but forms a mass, sometimes yellow and transparent, sometimes whitish and opaque. When obtained by fusion from the red protosulphide of phosphorus, it does not crystallize on cooling, unless it be first sublimed. After being fused and heated to the boiling point, it has a deeper colour, like that of sulphur. Its boiling point is higher than that of sulphur, and the colour of its vapour is a less intense yellow than that of sulphur vapour. When heated in the air, it burns with a pale phosphoric flame, and diffuses a large quantity of smoke. In moist air, it is decomposed almost as easily as tersulphide of phosphorus, and transformed into a white mass impregnated with phosphoric acid. It dissolves in caustic alkalis and in ammonia much in the same manner as a deliquescent salt dissolves in water. The solution has a pale-yellow colour: acids precipitate sulphur from it, and cause an abundant evolution of hydrosulphuric acid. It appears as if no alkaline sulphophosphate could exist in contact with water. The carbonates of potassa and soda slowly dissolve the pentasulphide of phosphorus in the cold, producing at the same time an abundant deposit of flakes of sulphur. On heating the liquid to about 60°, the sulphide of phosphorus dissolves with violence, and inodorous carbonic acid gas is evolved: no deposition of sulphur takes place. When boiled, the liquid evolves carbonic and hydrosulphuric acid gases together. The composition of pentasulphide of phosphorus is as follows:

	Calculation.		Berzelius.
P	31·4	28·19	28·06
5S	80·0	71·81	71·94
PS^5	111·4	100·00	100·00

(P^2S^5 = 2 . 196·14 + 5 . 201·17 = 1398·13. Berzelius.)

Combinations. Pentasulphide of phosphorus combines with sulphur-bases, forming salts called *Sulphophosphates.* One atom of it saturates 2 atoms of a sulphur-base, just as 1 atom of pyrophosphoric acid saturates 2 atoms of an oxygen-base: hence the sulphophosphates are the analogues of the pyrophosphates.

V. Persulphide of Phosphorus. PS^{12}.

Persulfure de phosphore, Phosphor-supersulfuret.

Preparation. When a small quantity of sulphur is dissolved, with the aid of heat, in liquid protosulphide of phosphorus, the persulphide is obtained on cooling, in the form of very regular crystals resembling those of sulphur. When 1 atom of protosulphide of phosphorus is fused at a temperature not exceeding 100° with 2 or 4 atoms of sulphur, nothing is obtained but these same crystals of persulphide, which collect at the bottom of the mother-liquid. When the quantity of sulphur amounts to four atoms, the whole solidifies in a mass on cooling: but on inclining the vessel, the protosulphide drains out drop by drop from the crystals of persulphide. If the temperature rises above 100° during the fusion, explosion takes place, and pentasulphide is formed: the explosion is most violent when 4 atoms of sulphur are used with 1 atom of the protosulphide. When a larger proportion of sulphur is used, the excess takes the form of plastic sulphur, and retains its softness and viscosity for a long time. It appears that the compounds PS^3 and PS^5 are never produced without powerful development of light and heat. This phenomenon is much less marked when the red modifications are operated upon; and hence it might appear to be due to a change of isomeric condition; but the facility with which the resulting compounds oxidize in the air is unfavourable to this hypothesis.

The best mode of obtaining the persulphide regularly crystallized, is to dissolve 1 atom of sulphur in 1 atom of liquid protosulphide of phosphorus by the heat of a water-bath, and then leave the vessel, carefully closed, to cool in the bath. The crystals thus obtained are few in number, but of considerable size, yellow and shining, and frequently present numerous facets, like those of native sulphur. Some are cleavable in the direction of the laminæ. They are impregnated with protosulphide of phosphorus, which adheres to them obstinately, and causes them to emit slight fumes from the surface of a recent fracture. To free the crystals from the protosulphide, they must be dried, reduced to small pieces, and placed between folds of bibulous paper under a bell-jar, and by the side of a small dish containing water. The edge of the bell-jar is slightly raised by the insertion of a small piece of wood, to allow of the renewal of the air within it. In this manner, the protosulphide adhering to the crystals is converted into phosphoric acid, sulphuric acid, and persulphide of phosphorus. Some time elapses before the change is complete; but sooner or later, the odour of the protosulphide disappears entirely. The crystals are then to be washed and dried over oil of vitriol.

The crystals thus obtained may be exposed to the air for a long time, without diminution of the lustre of the crystalline facets; but after a while, they redden litmus paper when placed upon it. In a stoppered bottle filled with dry air, they may be preserved for any length of time without alteration. They fuse at a temperature near the melting point of sulphur, and then distil over without separation of protosulphide of phosphorus. The distilled product does not crystallise, but remains soft long after cooling. If the persulphide, when subjected to distillation, is not quite free from protosulphide, an explosion takes place on the application of heat, arising from the formation of pentasulphide. This explosion, however, is not violent enough to break the vessel, unless the quantity of protosulphide retained in the crystals is considerable. But if the neck of the retort is merely inserted into the receiver, without luting, the retort is often thrown by the explosion to the distance of several feet.

The composition of persulphide of phosphorus is:

	Calculation.		Berzelius.
P	31·4	14·06	13·979
12S	192·0	85·94	86·021
PS^{12}	223·4	100·00	100·000

(P^2S^{12} = 2 . 196·14 + 12 . 201·17 = 2806·32. Berzelius.)

It dissolves in caustic alkalis, behaving like a mixture of sulphur and protosulphide of phosphorus. The products are phosphate and hyposulphite of potassa, together with persulphide of potassium.—By fusion at a gentle heat, persulphide of phosphorus may be made to take up an additional quantity of sulphur. ¶

[*Vid.* Berzelius, *Traité de Chimie, Par.* 1845, I., 815; also *Ann. Pharm.* 46, 129 and 251.]

B. Phosphuretted Sulphide of Carbon.—Bisulphide of carbon quickly dissolves eight times its weight of phosphorus, according to Trommsdorff, and twenty times its weight, according to Böttger, without becoming solid. Any white phosphoric matter or phosphoric oxide that may be mixed with the phosphorus remains undissolved*. The solution is specifically heavier than bisulphide of carbon, and refracts light more powerfully. The solution, covered with water and exposed to the sun's rays, becomes coated on the surface with a film of phosphoric oxide, yellow at first, but afterwards turning red; and when this is removed by a glass rod, a fresh film is formed,—and so on, continually, as long as any phosphorus remains in the solution. (Böttger.) According to Böckmann (*A. Tr.* 22, 2, 214), it is not reddened by exposure to sunshine. The greater the quantity of phosphorus contained in the solution, the lower is the temperature at which it takes fire: at 27° (49° F.), and on the addition of iodine or chlorine, which causes evolution of heat in combining with the phosphorus, the inflammation is instantaneous. (Brewster.) The vapour mixed with oxygen gas explodes on the approach of flame. Paper wetted with the solution takes fire spontaneously after some minutes

* The white and red modifications of phosphorus are insoluble in bisulphide of carbon: p. 110. [W.]

(Lampadius),—because, after the evaporation of the sulphide of carbon, the phosphorus remains behind in a state of minute division; the paper likewise takes fire when dipped in nitric acid. (Brewster.) A mixture of the solution with chlorate of potassa detonates violently on being rubbed, and is set on fire by contact with oil of vitriol. (Brewster.) If the bisulphide of carbon be distilled off out of contact of air, colourless phosphorus remains. (Lampadius.) A solution of 6 parts of phosphorus in one part of bisulphide of carbon deposits crystals at $-2 \cdot 5°$. (Trommsdorff.) Alcohol precipitates the phosphorus. (Berzelius.) One part of bisulphide of carbon coagulates with 21 parts of phosphorus into a mass of the consistence of goose-grease, which takes in a few seconds on bibulous paper, and sometimes, though not often, on glass or metal. (Böttger.—*Comp.* Lampadius, *A. Gehl.* 2, 195; Trommsdorff, *A. Tr.* 17, 1, 35; Brewster, *Edinb. Phil. J.* 5, 222; also *Schw.* 33, 121; Böttger, *Schw.* 68, 138; also *J. pr. Chem.* 12, 360.)

C. Sulphate of Phosphuretted Hydrogen.—Oil of vitriol absorbs phosphuretted hydrogen gas without immediate decomposition. (Buff.) The solution kept out of contact of air is decomposed in the course of four-and-twenty hours, with evolution of sulphurous acid, formation of phosphoric acid, and deposition of a yellow powder, consisting of sulphur free from phosphorus. (H. Rose.) According to Buff, however, it deposits phosphorus. The freshly prepared compound dropped into water immediately evolves non-spontaneously inflammable phosphuretted hydrogen gas, even though the spontaneously inflammable gas may have been used in preparing it; part of the gas remains absorbed by the watery liquid. (H. Rose.) Ammoniacal gas passed through the freshly prepared solution liberates a quantity of phosphuretted hydrogen equal to that which has been absorbed. (Buff, *Pogg.* 16, 366; H. Rose, *Pogg.* 24, 139.)

Anhydrous sulphuric acid is instantly decomposed by contact with phosphuretted hydrogen, without entering into combination with it. (H. Rose.)

¶ D. Sulphoxyphosphoric Acid. PO^3S^2.

Sulphophosphoric Acid.

Wurtz obtained this compound by the action of solution of caustic soda on the chloride of sulphur of Serullas, PCl^3S^2 (*vid.* Chap. X.). When the materials are put into a retort, and subjected to the heat of a water-bath, ebullition takes place, and part of the chloride distils over into the receiver. When the whole of the chloride has disappeared, the liquid in the retort is allowed to cool. It generally forms into a solid crystalline mass: this is to be drained, and the crystals purified by repeated solution in water and crystallization. The reaction is as follows:

$$PCl^3S^2 + 6NaO = 3NaO, PO^3S^2 + 3\ NaCl.$$

The soda must be in excess; because the free acid in solution is readily decomposed into phosphoric acid and sulphuretted hydrogen:

$$PO^3S^2 + 5HO = 3HO, PO^5, 2HS.$$

Sulphoxyphosphate of soda is readily soluble in boiling water, and crystallizes on cooling in brilliant six-sided tables. Its composition is

$3NaO, PO^3S^2 + 24HO$; analogous, therefore, to the ordinary tribasic phosphate: $3NaO, PO^5 + 24HO$. In fact, the acid may be regarded as phosphoric acid, in which 2 atoms of oxygen are replaced by sulphur; just as hypophosphorous acid (according to Wurtz) is phosphoric acid in which 2 atoms of oxygen are replaced by hydrogen (*vid.* p. 115). The solution of sulphoxyphosphate of soda has a strong alkaline reaction: chlorine, bromine, and iodine decompose it immediately, with separation of sulphur, and formation of ordinary phosphate of soda. The weakest acids added to the solution liberate sulphoxyphosphoric acid, which is immediately decomposed on boiling. The lime, baryta, and strontia salts are insoluble; the nickel and cobalt salts turn black on boiling; the lead-salt is white when newly formed, but turns black in a few hours, from separation of sulphide of lead. (Wurtz, *N. Ann. Chim. Phys.* 20, 472; abstr. *Ann. Pharm.* 64, 245.) ¶

OTHER COMPOUNDS OF SULPHUR.

A. With Selenium.—B. With Iodine.—C. With Bromine.—D. With Chlorine.—E. With Fluorine.

F. With Metals. *Metallic Sulphides, Sulphurets,* or *Sulphur-bases,* when they are electropositive,—*Sulphur-acids,* when they are electro-negative. (The compound of an alkali-metal with sulphur is also called *Liver of Sulphur. Hepar Sulphuris.*)

These compounds are, for the most part, formed according to the following proportions: 1 At. metal to 1, 2, 3, 4, or 5 At. sulphur,—and 2 At. metal to 1 or 3 At. sulphur.

Formation and Preparation of Anhydrous Metallic Sulphides. 1. By bringing the metal in contact with sulphur at ordinary or at higher temperatures. Finely divided copper (Zimmermann) and sodium (Winkelblech) combine with sulphur at ordinary temperatures on being rubbed with it. Several metals, as manganese, tin, lead, and nickel, combine with sulphur at its boiling point, and consequently burn in its vapour: others, as iron, do not combine with it below a red heat. The combination of a metal with sulphur is generally attended with vivid combustion, the sulphur playing with regard to the metal the same part that oxygen plays in ordinary cases of combustion. When sulphur is heated in a glass flask till the flask is filled with its vapour, thin leaves of copper or silver (Berzelius), tin or lead foil, and powdered manganese, nickel, or copper (Winkelblech) burn in it vividly. A piece of iron harpsichord wire also burns in the vapour, if a small piece of potassium or sodium be attached to its extremity to commence the combustion. (Winkelblech, *Ann. Pharm.* 21, 34.) If a piece of sulphur be thrown into a gun-barrel heated to redness at the lower end, and the vapour blown out at the touch-hole, a piece of wire, *e. g.* of iron, held in the vapour, burns with a bright light, and is converted into sulphide. (Hare.) Since the temperature at which sulphur combines with most metals is higher than its boiling point, the greater part of the sulphur evaporates before the metal has attained the temperature required for combination. To ensure combination in spite of this circumstance, the following methods may be adopted: (*a.*) The sulphur may be put into the lower part of the crucible—the metal, in the form of filings, *e. g.* iron-filings, into the upper part—the crucible covered, and surrounded in the air-furnace with dead

coals, and live coals heaped on the top of it,—so that the heat may pass from above downwards, and not bring the sulphur vapour in contact with the metal till the latter has attained the proper temperature. (*b.*) A small quantity of sulphur is placed at bottom, the mixture of metallic filings and sulphur placed upon it, and the crucible heated in a similar manner. (*c.*) The metal is heated to redness in a tube, and vapour of sulphur passed over it. (*d.*) The metal is heated with sulphur in a close vessel void of air; the sulphur is converted into vapour, and the vapour absorbed by the heated metal.

2. By heating a metal in hydrosulphuric acid gas, hydrogen being set free.

3. By igniting a metallic oxide with sulphur, whereby part of the sulphur is made to combine with the oxygen of the oxide and form hyposulphurous, sulphurous, or sulphuric acid, while the remaining portion combines with the metal. All fixed alkalies, either free or combined with carbonic acid (which is expelled without alteration during the process), yield, when ignited with sulphur, a mixture of 3 atoms of metallic sulphide and 1 atom of sulphate. (*Sch.* 37.)

$$4KO,CO^2 + 16S = 3KS^5 + KO,SO^3 + 4CO^2.$$

When hydrate of potassa is gently heated with sulphur, an alkaline hyposulphate and a metallic sulphide are produced. The heavy metallic oxides, on the other hand, disengage sulphurous acid when they are decomposed by ignition with sulphur: in such cases, they either give up the whole of their oxygen to one portion of the sulphur, and combine with the remainder to form a sulphide (oxide of copper, arsenious acid; $2\ AsO^3 + 9S = 2\ AsS^3 + 3SO^2$; *Sch.* 100; for A^s read As); or one part of the oxide, generally about half, remains undecomposed, and forms a peculiar compound with the sulphide produced (*e. g.* protoxide of manganese). Many metallic oxides undergo no change by ignition with sulphur; but when they are heated in contact with a mixture of equal weights of sulphur and carbonate of potassa (whereby pentasulphide of potassium is formed), gently at first, but afterwards, when the whole of the carbonic acid is expelled, kept for half an hour at a bright red heat in a covered porcelain crucible,—the mass, when cooled and digested in water, yields sulphide of potassium, while the other metallic sulphide remains undissolved, in the form of a shining crystalline powder. In this manner, Berzelius succeeded in forming the compounds of sulphur with cerium, chromium, and uranium. Part of the pentasulphide of potassium probably acts upon the oxide of the other metal, in such a manner as to form sulphate of potassa and the sulphide of the other metal.

4. By passing vapour of bisulphide of carbon over the metallic oxide at a red heat. The carbon unites with the oxygen of the metallic oxide to form carbonic oxide or carbonic acid, and the sulphur enters into combination with the reduced metal: *e. g.*

$$TiO^2 + CS^2 = TiS^2 + CO^2.$$

5. By decomposing a metallic oxide with hydrosulphuric acid.—For each atom of oxygen contained in the oxide, an atom of sulphur enters into combination with the metal. $PbO + HS = PbS + HO$; *Sch.* 41;—$Fe^2O^3 + 3HS = Fe^2S^3 + 3HO$;—$SnO^2 + 2HS = SnS^2 + 2HO$; *Sch.* 42;—$AsO^3 + 3HS = AsS^3 + 3HO$; *Sch.* 43;—$AsO^5 + 5HS = As$; *Sc.* 5 $+ 5HO$; *Sch.* 44.—*a.* The oxide is heated to redness, and hydrosulphuric acid passed over it. The sulphide thus produced often takes up more sulphur from the hydrosulphuric acid, and sets hydrogen

free (iron); sometimes also it absorbs the hydrosulphuric acid without decomposing it (potassium).—*b*. Hydrosulphuric acid gas is passed into water in which the metallic oxides or acids are diffused or dissolved. —*c*. The metallic acids or oxides are dissolved in an acid, and hydrosulphuric acid gas passed through the solution. In this manner,—even when one of the stronger acids is present in excess, provided it be not too concentrated—the oxides and acids of molybdenum, arsenic, antimony, tellurium, bismuth, cadmium, tin, lead, copper, and of the noble metals, are decomposed. A precipitate is formed, consisting of a pure anhydrous sulphide of the metal, and never containing undecomposed oxide—except in the case of red oxide of mercury, the salts of which—when the hydrosulphuric acid is not used in excess—are partly precipitated in the undecomposed state, together with the sulphide. The reaction between many metallic oxides and hydrosulphuric acid takes place at ordinary temperatures (oxide of lead)—viz. when hydrosulphuric acid, either in the gaseous state or dissolved in water, is brought in contact with the oxide, either free or dissolved in an acid: in other cases, a higher temperature is required (tungstic acid). With metallic oxides dissolved in water, *e. g.* the alkalis, hydrosulphuric acid forms solutions in which either a hydrated metallic sulphide or a hydrosulphate of the oxide may be supposed to exist: these solutions evaporated out of contact of air yield anhydrous sulphides.

6. Hydrogen gas or charcoal is made to act at a red heat upon metallic hyposulphites, sulphites, or sulphates (pp. 172—190).

$$KO,SO^3 + H = KS + 4HO \quad \text{(Sch. 84.)}$$
$$PbO,SO^3 + 2C = PbS + 2CO^2.$$

7. By double affinity: the solution of a heavy metallic salt is precipitated by a solution of the sulphide of an alkali-metal. The sulphide of the alkali-metal may contain 1, 2, 3, or 5 atoms of sulphur, and a corresponding number will be transferred to the heavy metal; and as the metal may not be capable of uniting with sulphur in all these proportions, uncombined sulphur may be precipitated together with the metallic sulphide. A solution of monosulphide of potassium, for example, precipitates a monosulphide of the metal from a solution of a heavy metallic oxide containing 1 atom of oxygen to 1 metal:

$$KS + PbO,NO^5 = PbS + KO,NO^5;$$

or if we suppose that monosulphide of potassium when dissolved in water is converted into hydrosulphate of potassa:

$$KO,HS + PbO,NO^5 = PbS + KO,NO^5 + HO:$$

further:

$$3KS + Fe^2O^3,3SO^3 + 3HO = Fe^2S^3,3HO + 3(KO,SO^3);$$
$$\text{or, } 3(KO,HS) + Fe^2O^3,3SO^3 = Fe^2O^3,H^3S^3 + 3(KO,SO^3):$$

The precipitate consists of hydrated sesqui-sulphide or iron, of ter-hydrosulphate of ferric oxide:—finally:

$$KS^5 + HgCl = KCl + HgS + 4S.$$

Metallic sulphides are solid and brittle (the sulphides of copper and silver alone possess a certain degree of ductility): they are generally crystalline. Their specific gravity is often below the calculated mean. The light metallic sulphides are pale yellow or brown, and without metallic lustre: the heavy ones are of various colours, mostly dark: some of them are transparent without metallic lustre (*Blendes*); others opaque, and possessed of metallic lustre. (*Pyrites, Glances*). The sulphides of the easily fusible metals are less fusible—those of the more refractory

metals, more fusible than the metals themselves. Sulphides are mostly less volatile than the pure metals.

Decomposition of Metallic Sulphides. 1. Some metals give up their sulphur at a moderate heat (gold); others retain it even at the highest temperatures (zinc); or if they are combined with more than one atom of sulphur, give up only a part of it (iron, tin).—2. Dry oxygen gas does not act on metallic sulphides at ordinary temperatures; the same gas when moist slowly converts several of them (iron) into sulphates. Exposed to the air or oxygen gas at high temperatures, they yield either sulphurous acid gas and metal (silver), or sulphurous acid gas and oxide (antimony, *Sch.* 28, bismuth, tin, and likewise iron when the heat applied is very great); or else a sulphate (the alkali-metals; also iron and copper at a very low red heat, *Sch.* 30). When heated in a glass tube open at both ends, they yield sulphurous acid, which may be detected by its odour, and by the bleaching of a piece of moistened logwood paper introduced into the tube. Heated with carbonate of soda upon charcoal, they yield a mass which, when moistened, blackens silver on which it is laid, and evolves sulphuretted hydrogen when acted upon by acids.—3. By nitric acid, and still more easily by aqua regia, most metallic sulphides are resolved into oxide, sulphur, and sulphuric acid: fuming nitric acid acts on them with peculiar violence, sometimes with evolution of light and heat. Hypochlorous acid and its salts likewise produce metallic oxide and sulphuric acid.—4. Chlorine acts upon many metallic sulphides, sometimes even at ordinary temperatures, in such a manner as to form chloride of sulphur and a metallic chloride.—5. Hydrated acids, even dilute nitric acid, resolve many metallic sulphides into hydrosulphuric acid and a salt. In the case of a hydrogen-acid, the action takes plase thus:

$$SbS^3 + 3HCl = SbCl^3 + 3HS:$$

in that of an oxygen-acid, we have for example:

$$CaS + SO^3 + HO = CaO,SO^3 + HS.$$

Warm concentrated hydrochloric acid decomposes in this manner, even the tersulphide of antimony, the sesqui-sulphide of bismuth, and the protosulphides of cadmium, lead, and tin. Hydrochloric acid gas acts upon most metallic sulphides so as to form hydrosulphuric acid and a metallic chloride: sometimes the aid of heat is required.—6. Alkalis, both in the dry and in the moist way, decompose many heavy metallic sulphides, the products of the decomposition being a sulphide of the alkali-metal and a heavy metallic oxide, which often enter into new combinations.—7. Hydrogen gas at a red heat only, decomposes the sulphides of antimony, bismuth, tin, copper, and silver, into hydrosulphuric acid and metal. (H. Rose, *Pogg.* 4, 109.)—8. Charcoal at an intense red heat, robs certain metallic sulphides of part or the whole of their sulphur, and forms bi-sulphide of carbon.

Most heavy metallic sulphides remain unaltered in water. Only the sulphides of molybdenum, tungsten, and arsenic are, when finely divided, slightly soluble in water, and are precipitated from it by acids, even by hydrosulphuric acid. (Berzelius.) When vapour of water is passed over metallic sulphides at a strong red heat, they are often resolved into hydrosulphuric acid and a metallic oxide, the latter of which often acts upon the rest of the sulphide in such a manner as to form reduced metal and sulphurous acid. (Regnault.) Sulphide of aluminum and sulphide of silicium in contact with water at ordinary temperatures produce hydrosul-

phuric acid and metallic oxide. The sulphides of barium, strontium, and calcium, are resolved with water into alkali, which, on account of its sparing solubility, crystallizes out first, and a hydrated double sulphide of the metal and hydrogen (*gewässertes Hydrothion-Schwefelmetall*), or, what comes to the same thing, a bi-hydrosulphate of the alkali. When the protosulphides of potassium and sodium are brought in contact with a small quantity of water, great heat is evolved, and an oily or a crystalline compound formed, which is soluble in a larger quantity of water. The solution may be regarded as containing either a hydrated protosulphide of the metal, or a simple hydrosulphate of the alkali, or perhaps also as a mixture of free alkali with a double sulphide of the metal and hydrogen (or bi-hydrosulphate of the alkali). Pentasulphide of potassium or sodium dissolves in water, with production of cold, and forms a solution containing either a hydrated metallic pentasulphide, or an alkaline hydrosulphite.

Compounds of Metallic Sulphides with water, which may also be regarded as salts of *Hydrosulphuric acid, Hydrosulphates*, or *Sulfhydrates.*

a. Hydrosulphates of the Alkalis, including Ammonia.

α Simple Alkaline Hydrosulphates or *Hydrated Metallic Protosulphides.*

These compounds are obtained:—1. By bringing the protosulphides in contact with water: *e.g.* $KS + HO = KO,HS$.—2. By passing hydrosulphuric acid gas through water in which the base is dissolved or diffused. According to the experiments of H. Rose, the existence of the simple hydrosulphates of baryta, strontia, or lime, is doubtful. On saturating the liquid with hydrosulphuric acid, each atom of base takes up 2 atoms of that acid, and there is formed, according to one theory, a double sulphide of the metal and hydrogen:

$$KO + 2HS = KS, HS + HO;$$

or, according to the other view, a bi-hydrosulphate of the alkali, viz., $KO,2HS$. By the addition of a fresh quantity of the base equal to that used in the first instance, this compound may be converted into pure hydrated metallic sulphide, or into a simple hydrosulphate of the alkali.

The alkaline hydrosulphates are either crystalline or oily, colourless, soluble in water, strongly alkaline, corrosive, have a sharp and bitter taste, and smell of hydrosulphuric acid, inasmuch as that gas is slowly evolved from them by the action of carbonic acid contained in the air. Hydrosulphate of ammonia volatilizes when heated; the other alkaline hydrosulphates, heated out of contact of air, either leave a protosulphide of the metal (potassa), or evolve hydrosulphuric acid and leave alkali (lime). Their aqueous solution boiled with sulphur takes up 4 atoms more of that substance, and is converted into solution of metallic pentasulphide or of alkaline hydrosulphite:

$$KS + 4S = KS^5; \text{ or } KO, HS + 4S = KO, HS^5.$$

By exposure to the air, the dissolved compounds are gradually oxidated; at first assuming a yellow colour, and being converted into metallic pentasulphides or alkaline hydrosulphites, with excess of alkali.

$$5KS + 4O = KS^5 + 4KO;$$
$$\text{or: } 5(KO, HS) + 4O = KO, HS^5 + 4KO + 4HO.$$

This compound is converted by further oxidation into an alkaline hyposulphite, then into sulphite, and finally into sulphate.

$$KS^5 + 4KO + 16O = 5\,(KO, SO^2.)$$

The alkaline hyposulphite is quickly formed by boiling the solution in the air, especially if an alkaline carbonate be present. This explains the occurrence of alkaline hyposulphites in hepatic mineral waters after they have been boiled down. (Fuchs, *Kastn. Arch.* 7, 101; L. A. Buchner, *Repert.* 61, 19.) Water containing air acts in the same manner by virtue of the oxygen which it has absorbed, but the action is slow at ordinary temperatures. If sulphide of sodium is dissolved in water containing air, and filtered after half an hour through acetate of lead, the liquid on being boiled yields a gaseous mixture, containing 26·6 per cent. of oxygen: if the precipitation be deferred for 4 hours, the gaseous mixture then evolved still contains 6 per cent. of oxygen; and if the water has a temperature of 87·5° and the precipitation is performed after half an hour, the gaseous mixture is found to contain only 4·8 per cent. of oxygen. (Anglada, *Ann. Chim. Phys.* 20, 260.) Small quantities of sulphurous acid cause a precipitation of sulphur, and produce a mixture of alkaline hyposulphite and hydrosulphite: with larger quantities, the former salt only is produced. Black oxide of manganese acts in a similar manner by virtue of the oxygen which it contains. A small quantity of chlorine produces a chloride and pentasulphide of the metal, or a hydrochlorate and hydrosulphite of the alkali: *e. g.*

$$5KS + 4Cl = 4KCl + KS^5$$
$$\text{or: } 5(KO, HS) + 4Cl = 4(KO, HCl) + KO, HS^5.$$

Excess of chlorine decomposes the water, the hydrogen of which it takes up, and, in the case of potassa and soda, produces a metallic chloride and an alkaline bisulphate:

$$2KS + 7HO + 8Cl = KO, 2SO^3 + KCl + 7HCl.$$

Acids added in small quantity, even the weakest, such as carbonic acid —provided they do not bring about another decomposition by oxidation— convert the simple alkaline hydrosulphates into bi-hydrosulphates; and, when added in larger quantity, expel the whole of the hydrosulphuric acid from the latter.

β. *Bi-hydrosulphates* of the *Alkalis*, including magnesia and ammonia, or *Hydrated Double Sulphides of Hydrogen and the Alkali-metals:* called *Sulfhydrates* by Berzelius, *Sulfhydrurets* by Rose.

These compounds are obtained: 1. By bringing a double sulphide of hydrogen and an alkali-metal in contact with water.—2. By passing hydrosulphuric acid gas to saturation through water in which the base is dissolved or diffused (p. 225). They are colourless, and mostly crystallizable. When heated out of contact of air, they either sublime (ammonia), or leave the corresponding anhydrous double sulphides (potassa, soda, lithia);

$$KO, 2HS = KS, HS + HO;$$

or they evolve hydrosulphuric acid, and leave metallic oxide. (The earthy alkalis and magnesia.) When dissolved in water, they are converted, by boiling with sulphur, into hydrated metallic pentasulphides or alkaline hydrosulphites, the change being attended with the evolution of half their hydrosulphuric acid. They also give up half their hydrosulphuric acid, when they form precipitates with solutions of the normal sulphate of protoxide of manganese, or of iron, or with sulphate of zinc. By this character they are distinguished from the simple alkaline hydrosulphates, which precipitate the sulphates just mentioned—provided no excess of acid is present—without emitting an odour of sulphuretted hydrogen. All

acids expel the hydrosulphuric acid contained in these salts. Between carbonic acid and hydrosulphuric acid, reciprocal affinity comes into play. (I., 126.) When carbonic acid gas is passed through the solution of an alkaline hydrosulphate, a bicarbonate is formed, and all the hydrosulphuric acid gradually driven out. From a solution of bi-hydrosulphate of lime, carbonic acid liberates the hydrosulphuric acid, and precipitates neutral carbonate of lime, which is afterwards converted into bicarbonate and dissolved. (L. A. Buchner.) If, on the other hand, hydrosulphuric acid gas be passed through water in which bicarbonate of ammonia, potassa, soda, baryta, strontia, lime, or magnesia, is dissolved or diffused, an alkaline bi-hydrosulphate is at first produced, together with a bicarbonate; the latter may, however, be completely decomposed by passing the gas through the liquid for a considerable time. The quantity of hydrosulphuric acid gas required to decompose a carbonate completely, is greater than the quantity of carbonic acid gas required to decompose a hydrosulphate. In both cases, a large excess of the decomposing acid is necessary; for the adhesion of the one gas to the other is one of the forces by which the decomposition is effected. When an aqueous solution of 1 At. baryta or lime is brought in contact with a mixture of 1 At. carbonic acid and 1 At. hydrosulphuric acid gas, neutral carbonate of baryta or lime is precipitated, and the water dissolves bicarbonate and bi-hydrosulphate of baryta or lime. The greater the excess of either gas, the larger is the quantity of the corresponding salt produced. Hence it may be concluded that all sulphuretted waters which contain an alkaline carbonate with excess of carbonic acid, do not contain all their hydrosulphuric acid in the free state, but a small portion in the form of an alkaline bi-hydrosulphate. (Fuchs, *Kastn. Arch.* 7. 101; O. Henry, *J. Chim. Med.* 1, 257 and 320; Gay-Lussac, *Ann. Chim. Phys.* 30, 291; also *N. Tr.* 12, 2, 260; L. A. Buchner, *Repert.* 61, 19.) The statement of Vauquelin (*J. Pharm.* 11, 124) and O. Henry, that bicarbonate of lime or baryta is not decomposed by hydrosulphuric acid, is disproved by L. A. Buchner: the decomposition is, however, very slow.

b. Hydrosulphates of the Heavy Metallic Oxides.

When a salt of protoxide of manganese, oxide of zinc, protoxide or binoxide of tin, protoxide or sesqui-oxide of iron, protoxide of cobalt, or oxide of nickel, is precipitated by the aqueous solution of a simple hydrosulphate or bi-hydrosulphate of an alkali, the precipitate (the formation of which, in the case of a nickel-salt, is attended with evolution of sulphuretted hydrogen) consists, not of anhydrous metallic sulphide, but of a compound which may be regarded either as a hydrated sulphide of the metal, or as a hydrosulphate of the oxide. In the case of protoxide of iron, it is $FeS + HO$ or FeO,HS; with the sesqui-oxide, $Fe^2S^3 + 3HO$ or $Fe^2O^3 + 3HS$; with protoxide of tin, $SnS + HO$, or SnO,HS; with binoxide of tin; $SnS^2 + 2HO$ or $SnO^2 + 2HS$. These precipitates often differ greatly in colour from the corresponding anhydrous sulphides; *e. g.* MnS is dark green; $MnS + HO$, flesh-coloured. They are tasteless and inodorous. Heated out of contact of air, they evolve water, and leave anhydrous metallic sulphide. By exposure to the air at ordinary temperatures, many of them, that of iron for example, are oxidized and converted either into a mixture of oxide and sulphur, or into a compound of the oxide with sulphuric acid. When digested with any of the stronger acids, all of them, excepting the hydrated bisulphide of tin, evolve hydrosulphuric acid. They are insoluble in water.

c. *Hydrated Metallic Pentasulphides*, or *Salts of Hydrosulphurous acid*, *Hydrosulphites*, *Compounds of Persulphide of Hydrogen*, *Sulfures hydrogénés*, *Hydrosulfures sulfurés*, *Hydrosulfates sulfurés*. [For the formation and preparation of these compounds, *vid.* p. 193.] The alkaline hydrosulphites are the only salts of this class that have been formed: the ammonia-compound has been obtained in the crystalline state, the others only in the state of aqueous solution.

Red-brown, or when considerably diluted, orange-yellow liquids—smelling slightly of hydrosulphuric acid—having a caustic, alkaline, and somewhat bitter taste, alkaline reaction, and corrosive properties.

The solution becomes colourless by exposure to the air, a hyposulphite being formed and sulphur precipitated at the same time:

$$KS^5 + 3O = KO, S^2O^2\ 3S$$

$$\text{or: } KO, HS^5 + 3O = KO, S^2O^2 + 3S + HO;$$

hence the liquid is rendered turbid by mixture with aërated water. If, however, the solution contains free alkali, no sulphur is precipitated, and the hyposulphite first formed is converted into sulphite, and ultimately into sulphate (Gay-Lussac & Welter):

$$KS^5 + 4KO + 16O = 5(KO, SO^3.)$$

Sulphurous acid and alkaline sulphites give rise to the formation of hyposulphites, with precipitation of sulphur. Peroxide of manganese produces a similar action. Nitric acid in excess takes up the alkali, oxidates the hydrogen of the hydrosulphurous acid, and precipitates the sulphur. Other acids, such as hydrochloric or sulphuric acid, which do not give up oxygen, separate the hydrosulphurous acid in its own proper form, provided they are made to act at once in large excess; but if they are added to the solution in successive small portions, the undecomposed portion of the hydrosulphite exerts an instantaneous decomposing action on the separated hydrosulphurous acid (p. 193), so that sulphuretted hydrogen gas is evolved and one atom of sulphur precipitated. Hydrosulphuric acid gas passed through the solution precipitates four atoms of sulphur, and produces an alkaline bi-hydrosulphate. Mercury, silver, and other metals, withdraw four atoms of sulphur from the solution, so that a hydrated protosulphide of the metal or a simple hydrosulphate of the alkali is left behind.

Compounds of Metallic Sulphides with Bisulphide of Carbon. *Sulpho-carbonates* of Berzelius. In combination with water they may likewise be regarded as *Hydro-sulphocarbonates*. The potassium-compound, for example, is KS, CS^2, or KCS^3: if one atom of water be added to it, the resulting compound may be considered as: $KO, CS^2, HS = KO, HCS^3$.

Preparation. 1. The hydrated protosulphide of an alkali-metal (or simple alkaline hydrosulphate) is brought in contact with bi-sulphide of carbon in a close vessel at a temperature of 30°: the sulphide of carbon quickly dissolves, forming a brown solution. (Berzelius.) Aqueous solutions of the fixed alkalis yield the same compounds with bisulphide of carbon; but the action is slower, and the product is mixed with alkaline carbonate. Solution of ammonia gives a mixture of hydro-sulphocarbonate and sulph-hydrocyanate of ammonia. (Zeise, p. 204.) Aqueous solutions of double sulphides of metals and hydrogen, or of metallic pentasulphides do not dissolve bisulphide of carbon. (Berzelius.)—2. Hydro-sulphocarbonic acid is mixed with a caustic alkali or an alkaline carbonate. Carbonic acid is then evolved. By evaporating certain solutions obtained by

(1) or (2), at temperatures below 40°, the anhydrous compounds of bisulphide of carbon with the metallic sulphides are obtained.—3. Solutions of heavy metallic salts are precipitated by hydro-sulphocarbonate of ammonia or potassa. Oxide of copper digested in aqueous solution of hydro-sulphocarbonate of lime, is converted into double sulphide of carbon and copper, with precipitation of lime.

The anhydrous compounds are reddish-yellow, brownish-yellow, brown, or black; the hydrated compounds yellow. Those which are soluble have a taste which is first cooling, then peppery, and afterwards hepatic. (Berzelius.)

The potassium-compound heated out of contact of air is resolved into charcoal and metallic tersulphide ($KS, CS^2 = KS^3, + C$); the barium, strontium, and calcium compounds, and those of the heavy metals, evolve sulphide of carbon and leave metallic sulphide—the decomposition taking place, sometimes at ordinary, sometimes at higher temperatures ($PbS, CS^2 = PbS + CS^2$). If water is present, the action of heat gives rise to the formation of a variety of products, such as carbonic, sulphurous, and hydrosulphuric acid, and sulphur. The solutions of the alkali-compounds are resolved by boiling into alkaline carbonate and hydrosulphuric acid gas:

$$KS, CS^2 + 3HO = KO, CO^2 + 3HS.$$

The compounds of the alkalis and some of the earths are soluble in water. These solutions, when concentrated, are tolerably permanent in the air; but in the dilute state they are rapidly decomposed, sulphur being precipitated and a carbonate formed.

$$KS, CS^2 + 3O = KO, CO^2 + 3S:$$
$$\text{or: } KO, HCS^3 + 3O = KO, CO^2 + HO + 3S.$$

The concentrated solution mixed with one of the stronger acids forms a yellow milky substance, from which hydrosulphocarbonic acid gradually separates in the form of an oily liquid. Those compounds which are not of themselves soluble in water are rendered soluble by mixture with an alkali-compound. (Berzelius.) The solutions of the alkali-compounds give a yellowish-white precipitate with zinc-salts, lemon-yellow with cadmium-salts (Berzelius), red with lead-salts, brown with copper-salts, and yellow with salts of mercuric oxide. The last two precipitates turn black in a few hours, bisulphide of carbon being evolved and a metallic sulphide formed. Silver solutions are precipitated yellow when dilute (the precipitate soon turning brown, and afterwards black), and black when concentrated. (Zeise.)

Compounds of Metallic Sulphides one with another. *Metallic Sulphur-salts.*

Metallic sulphides may be divided, with reference to their relations one to another, into basic sulphides, or *Sulphur-bases*, and acid sulphides, or *Sulphur-acids*. A metal which forms an oxygen-base when combined with a certain number of atoms of oxygen, produces a sulphur-base by combination with an equal number of atoms of sulphur; and in a similar manner, the number of oxygen-atoms in a metallic acid agrees with the number of sulphur-atoms in the corresponding sulphur-acid. Thus, $KS, FeS, Fe^2S^3, Cu^2S, CuS$, &c., are sulphur-bases corresponding to the oxygen-bases $KO, FeO, Fe^2O^3, Cu^2O, CuO$; and $MoS^3, AsS^3, AsS^5, TeS^3, SnS^2$, &c., are sulphur-acids analogous to the oxygen-acids $MoO^3, AsO^3, AsO^5, TeO^3$,

SnO^2, &c. In the sulphur series, however, as in the oxygen-series, there is a gradual transition from the bases to the acids; and the sulphides which stand near the middle of the series, Fe^2S^3, for example, play the part of sulphur-acids towards those which are more strongly basic, and of sulphur-bases towards those which are more strongly acid than themselves.

Preparation of Sulphur-salts. 1. By dissolving the sulphur-acid in aqueous solutions of sulphides of the alkali-metals, *e. g.* AsS^3 in KS: the combination is often attended with development of heat. Instead of a sulphide of the alkali-metal, a double sulphide of hydrogen and the metal may be used, *e. g.* KS, HS: but in that case, hydrosulphuric acid is evolved with effervescence.—2. By passing hydrosulphuric acid gas through the solution of an oxygen-salt containing a metallic acid, or by heating the latter with bi-hydrosulphate of ammonia, till the excess of the latter and of the ammonia set free in the process is driven off. By the action of the hydrosulphuric acid, water is formed, the metallic oxide converted into a sulphur-base, and the acid into a sulphur-acid:

$$3KO, AsO^5 + 8HS = 3KS, AsS^5 + 8HO.$$

3. By fusing an alkaline carbonate with a sulphur-acid. The carbonic acid escapes; part of the alkali reacts on the sulphur-acid in such a manner as to form a sulphide of the alkali-metal and a metallic acid, and the result is a mixture of oxygen-salt and sulphur-salt.—4. By saturating the aqueous solution of a caustic alkali or an alkaline carbonate with a sulphur-acid. The reaction is the same as in the last case.—5. By bringing a metallic acid in contact with aqueous solution of sulphide of hydrogen and potassium. The quantity of hydrosulphuric acid present not being sufficient for the complete conversion of the metallic acid into sulphide, a portion of sulphide of potassium is likewise decomposed, and consequently the sulphur-salt produced is mixed with a potash-salt of the metallic acid.—6. Sulphur-salts having a sulphide of an earth-metal or of a heavy metal for their base, are obtained by precipitating an oxygen-salt of an earth-metal or heavy metal by a sulphur-salt of potassium or other alkali-metal.

Most sulphur-salts are decomposed by hydrated oxygen-acids and hydrogen-acids,—the sulphur-base being converted, with evolution of sulphuretted hydrogen, into a compound of oxygen-acid and metallic oxide, or into a haloid-salt, and the sulphur-acid separated:

$$3KS, AsS^5 + 3SO^3 + 3HO = 3(KO, SO^3) + AsS^5 + 3HS;$$

similarly:

$$3KS, AsS^5 + 3HCl = 3KCl + AsS^5 + 3HS.$$

But if the sulphur-salt has been prepared by method 3 or 4, and still remains mixed with the oxygen-salt produced at the same time, the sulphur-acid is precipitated by the oxygen or hydrogen-acid, just as in any other case; but no hydrosulphuric acid is evolved, because the metallic oxygen-acid present is by its action reconverted into sulphur-acid. From this mode of decomposition it might be inferred that the sulphur-acid was combined with the alkali in its own proper form, and not as a mixture of sulphur-salt and oxygen-salt: but the presence of an oxygen-salt in such solutions may be demonstrated by digesting them with hydrated oxide of copper; for the oxide of copper resolves sulphide of potassium, for example, into potash, and an insoluble sulphur-salt having sulphide of copper for its base, while the filtrate contains the metallic acid in combination with potash. (Berzelius.)

Many sulphur-salts are either capable of combining with water in definite proportions, or soluble in it. Such compounds may be regarded either as hydrated sulphur-salts, or as double hydrosulphates. For instance, Schlippe's salt in the crystallized state is either $3NaS, SbS^5 + 18$ Aq.: or $3(NaO,HS) + SbO^5,H^5S^5 + 10$ Aq. (*vid.* p.10, 2 and 3.)

Many metallic sulphides likewise combine with oxides, forming compounds called *Oxysulphides;* also with iodides and chlorides.

G. Sulphur likewise combines with several organic substances; *e. g.* alcohol, ether, volatile oils, fat, resin, &c., and is a constituent of certain organic compounds.

Chapter VII.

SELENIUM.

Berzelius. *Schw.* 23, 309 and 430; 34, 79. *Pogg.* 7, 242; 8, 423.
Mitscherlich. Selenic Acid. *Pogg.* 9, 623.
Muspratt. Salts of Selenious Acid. *Quart. Journ. of Chem. Soc. of London,* 2, 52.

Selène, Selen.

History. Selenium was discovered in 1817 by Berzelius, who thoroughly investigated most of its chemical relations. Selenic acid was discovered in 1827 by Mitscherlich.

Sources. In Riolite, as pure selenium, mixed with variable quantities of seleniferous sulphur, selenide of cadmium, and selenide of iron (Del Rio, *Phil. Mag. J.* 8, 261; also *Pogg.* 39, 526); as seleniferous sulphur, in Volcano, one of the Lipari islands (Stromeyer, *Pogg.* 2, 410); as selenide of lead (Zinken & H. Rose, *Pogg.* 3, 271, Kersten); as selenide of copper (Berzelius); as selenide of silver (H. Rose); as selenide of mercury (Del Rio; Tiemann & Marx, *Schw.* 54, 224); a selenide of copper and silver, or eukairite (Berzelius); as selenide of copper and lead (Selen-kupfer-blei and Selen-blei-kupfer. *H. Rose, Kersten*); as selenide of cobalt and lead (Stromeyer, *Pogg.* 2, 403); as selenide of mercury and lead (H. Rose); as selenide of sulphur and mercury (H. Rose, *Pogg.* 46, 315; Kersten, *Kastn. Arch.* 14, 127); as selenite of lead (Kersten, *Pogg.* 46, 265). Moreover, in very small quantities: in iron pyrites from Fahlun: seleniferous sulphur is obtained from this substance by distillation, and used at Gripsholm for the manufacture of English oil of vitriol; a seleniferous deposit is formed on the floor of the leaden chamber. (Berzelius.) In iron pyrites from Kraslitz in Bohemia (Buch & Wöhler, *Gilb.* 69, 264); green vitriol is formed from this substance, and used in the preparation of fuming oil of vitriol: when the fuming acid thus obtained is diluted with water, a precipitate of selenium is obtained. (L. Gmelin, *Gilb.* 65, 206.) In iron pyrites from Luckawitz in Bohemia: the sulphur obtained from this pyrites yields, when used in the preparation of English oil of vitriol, a seleniferous deposit on the floor of the leaden chamber, similar to that yielded by the Fahlun sulphur, and containing, according

to Lewenau (*Abhandl. über das Selen.* Wien, 1823), 7·8 per cent. of selenium (Schrattenbach; Scholz, *Schw.* 38, 231; Pleischl, 39, 348). In the pyrites from which oil of vitriol is prepared at Nordhausen and Bodenmais (Buch, *N. Tr.* 3, 1, 435; Müller, *Br. Arch.* 2, 325; H. v. Meyer, *Kastn. Arch.* 6, 332). In iron pyrites from Felsobanya, Rota, and Kapnik (Kersten, *Kastn. Arch.* 14, 133). In copper pyrites from the Paris mountain in the isle of Anglesea, and in the oil of vitriol prepared from it. (Edm. Thomson, *Ann. Phil.* 18, 52.) In copper pyrites from the Rammelsberg, near Goslar, which also forms a seleniferous deposit on the floor of the leaden chamber. (Sandorff & Otto, *Ann. Pharm.* 42, 345.) In vitreous copper pitch-blende. (Kersten.) In copper-bloom from Rheinbreitenbach, but not in that obtained from other localities. (Kersten, *Schw.* 47, 294; further, *Pogg.* 26, 492.) In uranium pitch-blende from Johanngeorgenstadt, and Schneeberg. (Kersten, *Pogg.* 26, 492.) In galena from Atwidaberg and Fahlun. (Berzelius.) In sulphide of molybdenum from Schlackenwald. (Pleischl.) In tellurium ores. (Berzelius, Scholz.)

Preparation. 1. From the seleniferous deposit in the sulphuric acid works at Gripsholm. This reddish deposit consists of selenium, sulphur, arsenic, zinc, tin, lead, iron, copper, and mercury. It is dried and made up with aqua regia into a paste, which is gently warmed till it begins to give out the odour of horse-radish, and then mixed with more aqua regia. After this, it is left to itself for 48 hours, by which time the reddish colour becomes changed to the greenish-yellow of impure sulphur, and the whole of the selenium dissolves. Water is then added—the oxide of lead precipitated by sulphuric acid—the liquid filtered—the precipitate washed for a considerable time—the dark-yellow filtrate mixed with the wash-water—and hydrosulphuric gas passed through it,—whereby a mixture of selenide of sulphur with the sulphides of copper, mercury, tin, and arsenic is precipitated, and iron and zinc are retained in solution. The dirty-yellow precipitate, after being washed and pressed, is digested in concentrated aqua regia, till the undissolved portion has assumed the yellow colour of sulphur; the solution is decanted; the greater part of the excess of acid driven off by evaporation; the residue (consisting of selenious acid, sulphate of copper, chloride of tin, chloride of mercury, and a small quantity of arsenic acid), mixed with small portions of caustic potash, which precipitates the oxides of copper, tin, and mercury; the alkaline liquid evaporated to dryness; the residue ignited in a platinum crucible to expel any remaining trace of mercury, then quickly pounded in a warm mortar, and mixed with at least an equal weight of sal-ammoniac; and the finely pounded mixture gradually heated in a glass retort, till all the sal-ammoniac is volatilized, or even to a higher temperature than is required for that purpose. Part of the selenium is carried over into the receiver together with the water and ammonia which are evolved; but the greater portion sublimes in the upper part of the retort; or, if the heat applied is not very great, remains behind together with the saline mass in the retort. This saline mass is dissolved in water, the selenium well washed on a filter, and distilled, after drying, in a glass retort. (Berzelius.) To save the small quantities of selenium contained in the ammoniacal distillate above mentioned, and in the filtered solution of the saline mass, the former is heated to expel the ammonia, then mixed with the latter, and the whole boiled with repeated additions of sulphurous acid, by which the selenium is precipitated. If the mercury has not been completely separated in the former part of the process, it is precipitated, together with the selenium, by

the sulphurous acid. If the arsenic has not been completely precipitated by the sulphuretted hydrogen, it sublimes, together with the selenium, on heating the mass with sal-ammoniac.

2. From the seleniferous deposit of Luckawitz. *a.* This substance is dissolved in hot caustic potash, and the liquid filtered and exposed to the air at a temperature of 22°. Hyposulphite of potassa is formed and selenium precipitated (the quantity amounting to $11\frac{1}{2}$ per cent. of the deposit). The remainder of the selenium ($\frac{1}{4}$ per cent.) is obtained by boiling the mother-liquid with a piece of sulphur. A trace of sulphur perhaps remains mixed with the selenium. Any metallic selenides that may be contained in the original substance are not dissolved by the caustic potash. (Berzelius, *Pogg.* 8, 423.) Brunner (*Pogg.* 31, 19) first distils the seleniferous deposit in a glass retort: a slightly acid watery liquid passes over, at the commencement; then a dirty yellow selenide of sulphur (amounting to 12 per cent. of the whole) mixed with charcoal, while a black powder remains behind.—α. The distilled selenide of sulphur coarsely powdered is then put into tolerably strong boiling caustic potash, in sufficient quantity to saturate the alkali; the solution is diluted with six times its bulk of water; filtered, in case of any deposition of sulphur, or of loosely aggregated charcoal taking place after long standing; and the liquid exposed to the air in a shallow dish, as long as graphite-like vegetations form in it, and fall in scales to the bottom. Since these scales may still contain sulphur, they are again dissolved in caustic potash, and the solution exposed to the air;—or they are dissolved in aqua regia; the excess of acid expelled by evaporation; the liquid diluted with water; and the selenium precipitated by warming with sulphurous acid. After the deposition of the crystalline scales, the first alkaline liquid still yields selenide of sulphur in scales and powder of a fiery red colour, and containing from 10 to 12 per cent. of selenium, which may be obtained in a state of purity by dissolving the selenide of sulphur in caustic potash and exposing the solution to the air. The sulphur which separates after the lapse of several weeks from the first alkaline liquid, likewise contains selenium, which may be separated in the same manner. At length the liquid retains but a trace of selenium, which may be separated by saturating with hydrochloric acid, dissolving the resulting precipitate in caustic potash, and exposing the liquid to the air.—β. The black pulverulent residue in the retort, consisting of quartz-sand, lead, iron, lime, alumina, charcoal, sulphur, and a trace of selenium, is heated in a crucible with an equal weight of nitre and three times its weight of common salt, till the black colour disappears; the residue is then exhausted with water. The filtrate, boiled with hydrochloric acid till the nitric acid is expelled, and then digested with sulphite of ammonia, yields an additional quantity of selenium. 100 parts of the seleniferous deposit yield 6·1 parts of selenium by α, and 1·2 parts by β, making together 7·3 parts of selenium. The selenium thus obtained is finally purified by distillation. (Brunner.)—*b.* The seleniferous deposit is heated in a tubulated retort with nitric acid, the acid which distils over being frequently poured back, and the distillation ultimately carried to dryness. The residue is then exhausted with boiling water—the liquid filtered—and the filtrate, after evaporation, mixed with sulphite of ammonia, which causes a precipitation of selenium. The precipitate, after being washed, first with cold and then with hot water, is dried and completely purified by distillation in a glass retort. (Scholz.) Similar to this is the method of Lewenau. (*Schw.* 47, 306.) According to Berzelius, however, both in this method and in that

of Scholz, certain metals, mercury, for example, may be precipitated together with the selenium.—*c.* The dried seleniferous deposit is introduced into a porcelain tube, and heated in a stream of dry chlorine gas, the heat being regulated so as not to allow the mass to fuse. The vapours of chloride of selenium and chloride of sulphur thereby evolved are received in a vessel containing water, attached to the further end of the tube; and the liquid, after being filtered from the deposited seleniferous sulphur, is mixed with sulphite of potassa to precipitate the selenium. By this method, first applied by H. Rose to the analysis of seleniferous minerals, the author has obtained pure selenium.—*d.* If the seleniferous deposit is rich in sulphur and poor in selenium, Magnus (*Pogg.* 20, 165) mixes it with eight times its weight of peroxide of manganese and heats the mixture to redness in a glass retort. The sulphur escapes as sulphurous acid—the selenium sublimes, partly in the free state, mixed however at the beginning with a little sulphur—partly in the form of selenious acid. The sulphurous acid gas is passed through water, and the selenious acid carried over with it is thereby reduced. The sublimed selenium is freed from sulphur by a second distillation with peroxide of manganese, or by solution in caustic potash and exposure to the air, or by solution in aqua regia and precipitation with sulphurous acid.—*e.* The seleniferous deposit or seleniferous sulphur may likewise be burned by means of an aspirator. The sulphur is then converted into sulphurous acid, while selenium containing but little sulphur sublimes: it may be purified by solution in potash. (Brunner.)

3. From Selenide of Lead.—*a.* The pounded ore is freed by digestion in dilute hydrochloric acid from calcspar and carbonate of iron, which may be mixed with it; then, after being washed and dried, it is intimately mixed with an equal weight of burnt tartar; and the mixture, covered with coarse charcoal-powder, is ignited for an hour in an earthen crucible at a moderate heat. The mass, after cooling, is quickly pounded in a warm mortar—the powder thrown on a filter, and washed with boiling water thoroughly freed from air, the washing being continued as long as the water which runs through exhibits any colour. The filter must all the while be kept quite full of water, to prevent the selenide of potassium from coming in contact with the air. The red-brown filtrate, exposed to the air in shallow dishes, becomes covered with a reddish-black crust of selenium: this crust must be frequently broken up till it no longer forms and the liquid becomes colourless. The precipitated selenium is washed on a filter, and freed by distillation from a small quantity of metallic selenide which may be mixed with it. The trace of selenium which remains dissolved in the alkaline liquid may be separated by warming the liquid with hydrochloric acid and sulphurous acid. From the powdered ore which remains on the first filter, a quantity of silver may be obtained amounting to 20 per cent. of the selenide of lead. (Wöhler, *Ann. Pharm.* 41, 122.) To detect traces of selenium in sulphur, galena, or iron pyrites, the substance may be fused with potash, the fused mass digested in water, and the filtered solution exposed to the air: selenium, if present, will then be precipitated. (Wehrle, *Zeitschr. Phys. v. W.* 3, 317.)—*b.* Native selenide of lead, pounded and freed from carbonates by digestion in hydrochloric acid, is mixed with an equal weight of nitrate of soda, and the mixture thrown by successive portions into a red-hot crucible. The fused mass when cold is boiled with water; the insoluble residue, which contains no more selenium, separated by filtration; and the solution containing seleniate, nitrate, and nitrite of soda, rapidly boiled down, nitric acid

being added to decompose the nitrite: crystals of anhydrous seleniate of soda are then deposited. The liquid poured off from the crystals while still hot deposits nitrate of soda on cooling; and if the solution poured off from this be once more boiled down, it again yields seleniate of soda. The liquid once more decanted off from the crystals yields a fresh portion of nitrate of soda,—and so on, till all the liquid is used up. The seleniate of soda thus obtained (slightly contaminated with sulphate) is mixed with sal-ammoniac and heated; and when the mass is exhausted with water, pure selenium remains behind. (Mitscherlich.)

4. From metallic selenides in general. Solution of selenic acid is prepared from these compounds, and saturated with potash; the residue obtained by evaporation is then mixed with an equal weight of sal-ammoniac, and the selenium sublimed in a glass retort. (Berzelius.)

5. From the Kraslitz oil of vitriol. This liquid is diluted with twice its bulk of water; the red precipitate freed from sulphuric acid by decantation and washing, and then dried; the selenium is obtained from it by distillation. A small quantity of inflammable oil is evolved in this process, and the black residue contains a lead compound, together with charcoal. The red precipitate contains a considerable quantity of gypsum, from which it must be freed by repeated washing in water. 100 parts of Bohemian oil of vitriol yield only from 0·005 to 0·007 of selenium. (Joss, *Schw.* 69, 333.)

Properties. Selenium crystallizes in four-sided prisms. From an aqueous solution of hydroseleniate of ammonia exposed to the air, Berzelius obtained selenium in square prisms; Frobel (*Pogg.* 49, 590) obtained it in rhombic prisms having their summits and lateral edges truncated, and apparently belonging to the right prismatic system. By sublimation, or by cooling a saturated solution of selenium in oil of vitriol, Frankenheim (*J. pr. Chem.* 16, 13) obtained prisms which appeared to be obliquely rhombic. Pleischl (*Kastn. Arch.* 4, 343) obtained by sublimation, acute crystals like those of sulphur; but as Berzelius (*Pogg.* 7,242), found that the crystals which he himself obtained by sublimation were really selenide of mercury, he suspects that something similar was the case with Pleischl's crystals. The specific gravity of selenium varies between 4·3 and 4·2. It is brittle, like glass, not hard, easily scratched and pulverized. A mass of it rapidly cooled from a state of fusion exhibits a red-brown, metallic-shining surface, and a conchoidal fracture, the freshly broken surfaces having a dark leaden-grey colour, and considerable lustre: after very slow cooling, it exhibits a granular, leaden-grey surface, and a dull, fine-grained fracture. When precipitated by dilute sulphurous acid from a very dilute solution of selenious acid, the solutions being cold and exposed to daylight, it appears as a golden yellow film: in a less finely divided state, as obtained from a less dilute solution, it forms a scarlet powder, which, when the liquid is warmed, aggregates to a denser powder, first of a dark red, and afterwards of a reddish black tint. Selenium solidified after fusion is reduced by trituration to a dark red powder, which, in those parts where it is pressed together and polished by the pestle, exhibits a grey colour and metallic lustre.

¶ According to Count Schaffgotsch (*J. pr. Chem.* 43, 308), the specific gravity of selenium rapidly cooled from fusion is 4·282; that of granular selenium, 4·801; and that of dark red precipitated selenium, and of the greyish black variety obtained by gently heating the latter, varies from 4·259 to 4·264. The specific gravity of the granular variety is to that of selenium rapidly cooled from fusion, as 112·1 : 100. ¶

Selenium softens when heated; becomes semifluid at 100°, and perfectly fluid at a somewhat higher temperature. As it cools, it remains soft for a long time, and may be worked like sealing-wax and drawn out into long, elastic, transparent threads. Boils below a red heat, somewhat below 700°. (Mitscherlich, *Pogg.* 29, 229). The colour of its vapour is yellow, darker than that of chlorine gas, but lighter than that of sulphur vapour. The vapour does not smell like horse-radish: in narrow vessels it condenses to metallic-shining drops; in large vessels, to scarlet flowers; and in the air, to a red cloud. Selenium is a bad conductor of heat, and a non-conductor of electricity, but it cannot be rendered electrical by friction. (Berzelius.) According to Knox, fused selenium conducts the electric current of a sixty-pair battery. According to Bonsdorff, selenium becomes electrical when rubbed in very dry air.

Compounds of Selenium.

Selenium and Oxygen.

Selenium exhibits less affinity for oxygen than sulphur: when gently heated in the air, it sublimes without change, and does not take fire till more strongly heated, *e. g.* by contact with flame; it then burns in the air with a reddish-blue flame, and in oxygen gas with a flame which is white below and bluish-green above,—and is converted, partially at least, into selenic oxide and selenious acid. (Berzelius.)

A. Selenic Oxide. SeO?

Formed, together with selenious acid, in the combustion of selenium in air or in oxygen gas; in small quantities, also, when selenium is heated in contact with selenious acid, both substances, however, subliming for the most part, without change. It is formed in larger quantity by heating sulphide of selenium with a mixture of nitric and hydrochloric acid, in which the quantity of nitric acid present is not sufficient for the complete oxidation of the selenium. From the selenious acid produced at the commencement of the action, the sulphur which still remains unoxidized again withdraws selenium. Selenic oxide gas is obtained, mixed with oxygen, by burning selenium in a vessel filled with oxygen gas, and removing the selenious acid, which is produced at the same time, by agitation with water.

Colourless gas, with an odour like that of horse-radish, and so strong and penetrating, that $\frac{1}{50}$ of a grain of selenium is sufficient to fill a room in which it is burned, with the odour. It does not redden litmus.

But slightly soluble in water, to which it imparts its odour, but no taste: by aqueous solutions of alkalis, it is absorbed only in proportion to the quantity of water present. Not precipitated from its solution in water by hydrosulphuric acid. (Berzelius.)

B. Selenious Acid. SeO^2.

Acide sélénieux, Selenige Säure: formerly called *Selenic acid.*

Formation. 1. When selenium is burnt in air or oxygen gas, the oxide being formed at the same time.—2. When selenium is treated with nitric acid or aqua regia, or with sulphuric acid and peroxide of manganese. (Berzelius.) Also when oil of vitriol is boiled with selenium.

(Gm.) Cold nitric acid has scarcely any action on selenium; but the same acid when heated acts vigorously on it;—aqua regia acts still more powerfully.

Preparation. When selenium is heated in a glass bulb till it boils, and oxygen gas passed over it, combustion ensues and selenious acid sublimes.—2. When selenium is dissolved in warm nitric acid or aqua regia, and the liquid heated in a retort, nitric and hydrochloric acids distil over at first, and subsequently selenious acid sublimes. (Berzelius.)

Properties. Sublimes in white, four-sided needles, often two inches long, and having a peculiar lustre,—or if the place where it is deposited is very hot, it forms a dense, white, translucent mass. Under the ordinary pressure of the air, it does not fuse when heated, but merely bakes together. Vaporizes just below the boiling point of oil of vitriol, and forms a vapour of the colour of chlorine gas. Its taste is purely acid at first, but afterwards burning. In the state of vapour it has a pungent, sour smell. (Berzelius.)

	Calculation.		Berzelius.
Se	40	71·43	71·21
2O	16	28·57	28·79
SeO^2	56	100·00	100·00

	Vol.	Sp. gr.	Vol.	Sp. gr.
Vapour of Selenium?	1	16·6392 =	$\frac{1}{6}$	2·7732
Oxygen gas	6	6·5558 =	1	1·1093
Vapour of Selenious acid	6	23·2950 =	1	3·8825

(SeO^2 = 494·58 + 200 = 694·58. Berzelius.)

Decompositions. 1. Selenious acid in combination with ammonia gives up its oxygen, under the influence of heat, to the hydrogen of the ammonia, so that nitrogen and selenium are set free.

$$3NH^3, 3SeO^2 = 6HO + NH^3 + 3Se + 2N.$$

The decomposition, however, is not complete: a quantity of gas, which appears to be hydroselenic acid, is evolved, and part of the selenious acid remains undecomposed, some of it passing over with the ammoniacal liquid, while the rest remains in the fixed residue. On this reaction depends the separation of selenium from selenite of potassa by heating that salt with hydrochlorate of ammonia, selenite of ammonia being first produced by double affinity.—2. Sulphurous acid, or an alkaline sulphite to which hydrochloric acid is gradually added, precipitates selenium from aqueous selenious acid in red or reddish-black flakes: at low temperatures and in the dark, the action is slow; but in direct sunshine, or when aided by heat, the precipitate is rapidly formed. (Berzelius.)

$$SeO^2 + 2SO^2 = Se + 2SO^3.$$

The precipitation is not completed in less than half an hour's boiling. If the mixture contains nitric acid, the selenium is not completely precipitated till the nitric acid is decomposed by the addition of a proper quantity of sulphurous acid: in such a case, therefore, it is better to free the liquid from nitric acid by previous evaporation with hydrochloric acid, and then treat it with sulphurous acid. (Berzelius.) Hyposulphite of ammonia, in the cold, precipitates only a trace of selenium mixed with sulphur; a larger quantity is separated on boiling, and still more on the

addition of hydrochloric acid. (H. Rose, *Pogg.* 33, 239.) In the cold, the decomposition takes place very slowly, if at all: on boiling, however, bisulphide of selenium is deposited:

$$SeO^2 + 2S^2O^2 = SeS^2 + 2SO^3:$$

the addition of aqua regia immediately decomposes the bisulphide of selenium. (Muspratt.)—3. Selenious acid mixed with hydrochloric acid deposits selenium upon iron and zinc, either in the form of a dark copper-coloured film, or in red-brown or blackish-grey flakes, according to the temperature. The deposit formed on iron is mixed with selenide of iron. Selenious acid behaves in a similar manner when mixed with other acids: when sulphuric acid is present, the selenium is deposited very slowly, and contains sulphur: if the liquid also contains arsenious acid, the precipitation is extremely slow. (Berzelius.) All the metals, from zinc up to silver (therefore neither gold, platinum, nor palladium), precipitate selenium from selenious acid mixed with sulphuric acid. Silver becomes covered with a film of selenide of silver, whence its surface assumes a yellow and brown tint: it exhibits this appearance even in liquids containing only from $\frac{1}{50,000}$ to $\frac{1}{10,000}$ of selenium. (Fischer, *Kastn. Arch.* 13, 228; *Pogg.* 10, 152.)—4. Selenious acid heated with selenium remains for the most part unaltered, only a small quantity being converted into selenic oxide.—5. Selenious acid doubtless gives up its oxygen, under the influence of heat, to hydrogen, carbon, boron, phosphorus, sulphur, organic substances, and many metals.—6. Hydrosulphuric acid and selenious acid form, by double decomposition, selenide of sulphur and water. (Berzelius.)

$$SeO^2 + 2HS = SeS^2 + 2HO.$$

The complete decomposition of selenious acid by hydrosulphuric acid is as difficult as that of arsenic acid by the same reagent. (H. Rose, *Pogg.* 42, 538.) Selenious acid is not decomposed in the slightest degree by boiling with hydrochloric acid. (Berzelius.)

Combinations. *a.* With Water. *α. Hydrate of Selenious acid.*—Crystallizes from a hot aqueous solution, on slow cooling, in large, longitudinally striated crystals, very much like those of nitre: by rapid cooling, it is obtained in small grains. It is also formed on exposing the crystals of the anhydrous acid to the air: these crystals lose their lustre as they attract moisture from the air, and stick together without becoming wet. The hydrate when heated first gives up its water, the anhydrous acid not subliming till the heat is considerably increased. (Berzelius.)

β. Aqueous Selenious acid. The acid dissolves very easily in cold water; in hot water it is soluble in almost all proportions. (Berzelius.)

b. With Salifiable Bases, selenious acid forms the class of salts called *Selenites.* Its affinity for salifiable bases is considerable; but in this respect it appears to be always inferior to sulphuric acid, and in most cases to nitric and hydrochloric acid also. It withdraws oxide of lead from hydrochloric acid, and the oxides of lead and silver from nitric acid. Among the selenites are salts containing one, two, and four atoms of acid to one of base: the number of basic selenites is but small. The normal alkaline selenites have always an alkaline reaction, and a taste not characteristic of the acid, but purely saline. The biselenites have an acid reaction. The protoxides of lead, copper, silver, and the di-oxide of mercury, do not combine with two atoms of selenious acid. If an alkali be combined with such a quantity of selenious acid as to form a solution neutral towards vegetable colours, this solution, when con-

centrated by evaporation, yields crystals of alkaline biselenite, while a normal salt remains in solution, and gives an alkaline reaction to the liquid. Selenites with four atoms of acid are found only among the alkalis.—Many metallic selenites, when heated, give up all their acid; others, as the lead-salt, only a part; others, again, give up none. The selenites, when ignited with charcoal, evolve carbonic oxide and carbonic acid gases without detonation, and are either converted into metallic selenides by giving up part of their selenium—as is the case with the selenites of the fixed alkalis and many heavy metallic oxides,—or they part with the whole of their selenium and leave metallic oxide, as is the case with the earthy selenites. (Berzelius.) The selenites fused upon charcoal with microsmic salt or carbonate of soda, in the inner blow-pipe flame, emit the odour of horse-radish. The mass obtained by fusion with carbonate of soda colours silver foil on the addition of water, in the same manner as that obtained with sulphates. (H. Rose.) Selenites ignited with sal-ammoniac in a glass tube or retort, yield a sublimate of selenium. Their solution in water or hydrochloric acid gives with sulphurous acid, in the cold, a red precipitate of selenium, but when heated, a grey precipitate. Their solutions in acids deposit upon zinc a coating of selenium, copper-coloured at first, but afterwards becoming brown and black. Mixed with aqueous hydrochloric acid, they give with sulphuretted hydrogen a precipitate of sulphide of selenium, which is yellow when formed in the cold, but yellowish red when separated at higher temperatures. When sulphuretted hydrogen gas is passed through aqueous solution of selenite of ammonia, potassa, or soda, the same reddish-yellow precipitate is formed; but it soon turns black-brown, because the monosulphide of the metal (or simple alkaline hydrosulphate) produced, abstracts sulphur from it, and is itself converted into pentasulphide of the metal (or alkaline hydrosulphite). On passing the hydrosulphuric acid gas through the solution for a longer time, sulphur is precipitated almost free from selenium, and the preceding compound is converted into a double sulphide of hydrogen and the metal (bi-hydrosulphate of the alkali). Boracic, phosphoric, and sulphuric acid, with the aid of heat, expel selenious acid from its salts. Hydrochloric acid has no action on the selenites. The normal selenites of ammonia, potassa, and soda, are soluble in water; the other normal selenites are nearly or quite insoluble; the biselenites and tetraselenites are easily soluble. All selenites are soluble in nitric acid; the lead and silver-salts, however, dissolve with difficulty. (Berzelius.) Hence those selenites which are soluble in water, give with baryta-salts a precipitate which is soluble in hydrochloric or in nitric acid. (H. Rose.)

c. Selenious acid is easily soluble in alcohol. (Berzelius.)

C. Selenic Acid. SeO^3.

Acide sélénique, Selensäure.

Formation. 1. When selenium, metallic selenides, selenious acid, or any of its salts, are ignited with nitrate of potassa or soda.—2. When chlorine gas is passed through solution of selenite of potassa mixed with free potassa. (Berzelius.) 3. When selenium or selenious acid is brought in contact with water and excess of chlorine (H. Rose), or with hypochlorous acid. (Balard.)

Not known in the separate state.

		Calculation.		Mitscherlich.
Se		40	62·5	61.4
3O		24	37·5	38·6
SeO^3		64	100·0	100·0

(SeO^3 = 494·58 + 3 . 100 = 794·58. Berzelius.)

Combinations. *a.* With Water. *Aqueous Selenic Acid.* 1. Selenium free from sulphur is dissolved in excess of nitric acid—the solution (which should not give a precipitate with chloride of barium, otherwise it contains sulphuric acid) saturated with carbonate of soda—the mixture evaporated to dryness—the remaining mixture of selenite and nitrate of soda fused in a porcelain crucible at a low red heat—the seleniate of soda separated from the nitrate in the manner described on page 234, 3, *b*—and the seleniate purified by recrystallization. It is then dissolved in water—the solution treated with nitrate of lead—and the precipitated seleniate of lead, after being well washed and diffused through water, decomposed by hydrosulphuric acid. Lastly, the solution is filtered and concentrated by evaporation. If the acid thus obtained will not volatilize completely, it contains soda-salt, in consequence of the seleniate of lead not having been thoroughly washed: in this case, it must be saturated with oxide of copper, the seleniate of copper purified by crystallization, and its aqueous solution decomposed by sulphuretted hydrogen. If it still contains sulphuric acid, it will give a precipitate with chloride of barium, after being boiled with nitric acid. Any nitric acid which may be mixed with it goes off during the process of concentration. (Mitscherlich.) Selenic acid may also be prepared by throwing a mixture of 1 part of selenium and 3 parts of nitre, by small portions at a time, into a red-hot crucible, in which it explodes, then dissolving the residue in water, precipitating with nitrate of baryta, &c.; or else, by mixing an aqueous solution of selenite of potassa with a quantity of potassa equal to that which it already contains—then saturating with chlorine gas—precipitating the resulting mixture of seleniate of potassa and chloride of potassium with a boiling solution of chloride of lead, washing the precipitate thoroughly, &c. (Berzelius.)—2. Chlorine gas is passed in excess through aqueous selenious acid:

$$SeO^2 + Cl + HO = SeO^3 + HCl;$$

or chlorine gas is slowly passed over moistened selenium-powder, which is frequently stirred about till the selenium is converted into bichloride; the solution is then largely diluted with water, more chlorine passed through it, and the excess of chlorine allowed to escape by exposure to the air. In this manner, a dilute solution of selenic and hydrochloric acid is obtained: it cannot, however, be concentrated by evaporation without being reconverted into selenious acid and chlorine. (H. Rose, *Pogg.* 45, 337.)

The concentrated aqueous solution of selenic acid is a transparent and colourless liquid. When evaporated till the temperature reaches 165° (329° F.) its specific gravity is 2·524: if the concentration be continued till the temperature rises to 267° (512·6° F.) the specific gravity is increased to 2·600; and after further concentration to 285° (545° F.), in which case, part of the acid becomes changed into selenious acid, the specific gravity becomes equal to 2·625. The acid evaporated to 280° (536° F.) contains 84·21 per cent. of acid to 15·75 of water, or rather more than 1 atom of water to 1 atom of acid. The tendency to decomposition

at high temperatures, prevents the formation of the pure hydrate. (Mitscherlich.)

When heated above 285°, selenic acid is resolved into oxygen and selenious acid. When it is boiled with hydrochloric acid, chlorine gas and selenious acid are produced; and a mixture of selenic and hydrochloric acid dissolves gold and platinum, as aqua regia does. Aqueous selenic acid, with the aid of heat, dissolves copper and gold—but not platinum—and is reduced to the state of selenious acid; zinc and iron are dissolved by it, with evolution of hydrogen gas. It is not decomposed either by sulphurous or by hydrosulphuric acid. The concentrated acid, when mixed with water, evolves as much heat as oil of vitriol does; it also absorbs moisture from the air. (Mitscherlich.)

b. With Salifiable Bases: *Seleniates.* The affinity of selenic acid for salifiable bases is almost as great as that of sulphuric acid. The seleniates are isomorphous with the sulphates, chromates, and manganates. Most of them sustain a red heat without decomposition. They detonate on glowing charcoal (Mitscherlich), emitting an odour of selenium, and generally leaving a metallic selenide. (Berzelius.) Heated before the blowpipe with microcosmic salt or carbonate of soda, they exhibit the same appearance as the selenites. (H. Rose.) The seleniates are reduced to selenides by hydrogen gas at a temperature much lower than that which is required for the reduction of sulphates to sulphides. (Berzelius.) When heated with sal-ammoniac, they are reduced, with separation of selenium. Boiled with hydrochloric acid, they yield selenious acid and chlorine (whereby they acquire the power of dissolving gold, and decolorizing tincture of indigo), whence they become decomposible by sulphurous or hydrosulphuric acid (which separate selenium or selenide of sulphur from them), and no longer give a precipitate with chloride of barium. (Mitscherlich.) The insoluble seleniates require long boiling with hydrochloric acid to decompose them in this manner. (H. Rose.) The selenic acid contained in them is not decomposed by sulphurous or hydrosulphuric acid. All normal seleniates are soluble in water, excepting the baryta, strontia, and lead salts, which are nearly or quite insoluble in water and in aqueous nitric acid. (Hydrochloric acid may exert a gradual solvent action by reducing the selenic to selenious acid.) Hence the soluble seleniates give with baryta salts a precipitate insoluble in acids.

Selenium and Hydrogen.

Hydroselenic Acid. HSe.

Seleniuretted Hydrogen, Selenide of Hydrogen, Hydroselen, Selenwasserstoff, Wasserstoff-Selenid, Hydroselensäure, Acide hydrosélénique, Acide Sélénhydrique, Sélénide hydrique;—and in the gaseous state: *Hydroselenic acid gas, Seleniuretted Hydrogen gas, Hydroselengas, Selenwasserstoffgas, Gas acide hydroselenique, &c.*

Formation. In the decomposition of a metallic selenide by a hydrated acid. (Berzelius.) According to Pleischl (*Kastn. Arch.* 4, 339), a small quantity of hydroselenic acid is likewise evolved in the sublimation of selenium moistened with water.

Preparation. Dilute hydrochloric acid is poured upon selenide of

potassium or selenide of iron, and the evolved gas collected over mercury. (Berzelius.)

Properties. Colourless gas. Sp. gr. (*vid.* I., 279). Smells at first like hydrosulphuric acid; but subsequently produces dryness, and a pungent, astringent, and painful sensation in all parts of the mucous membrane of the nose with which the gas has come in contact: a bubble of the gas no larger than a pea produces inflammation of the eyes; destroys the sense of smell for several hours; and frequently brings on a cold in the head, or a dry painful cough, which lasts for a fortnight.

	Calculation.		Berzelius.
Se	40	97·56	97·56
H	1	2·44	2·44
HSe	41	100·00	100·00

	Vol.	Sp. gr.	Vol.	Sp. gr.
Vapour of Selenium	1	16·6392	$\frac{1}{6}$	2·7732
Hydrogen gas	6	0·4158	1	0·0693
Hydroselenic acid gas	6	17·0550	1	2·8425

($H^2Se = 2 . 6·24 + 494·58 = 507·06$. Berzelius.)

Decompositions. 1. Hydroselenic acid gas, in contact with moist substances and with air, forms water and selenium, which, when the bodies are porous, like wood or paper, colours them red throughout their substance. (Berzelius.)—2. One volume of hydroselenic acid gas, in contact with heated tin, produces selenide of tin and one volume of hydrogen gas. Hydroselenic acid gas collected over impure mercury is also converted, in the course of a week, into hydrogen gas—the mercury becoming covered with a copper-coloured deposit. (Bineau, *Ann. Chim. Phys.* 67, 230; 68, 424.)

Combinations. a. Aqueous Hydroselenic Acid, Seleniuretted Hydrogen Water. Water absorbs hydroselenic acid gas more abundantly than hydrosulphuric acid. To observe the absorption, water freed from air by boiling is passed up into the gas standing over mercury. The solution is a colourless liquid of faint odour and hepatic taste; it reddens litmus and produces a permanent dark-brown stain on the skin. When exposed to the air, it becomes turbid and red, the change progressing from above downwards; at length, complete decomposition ensues, and the selenium is precipitated in red flakes. A small quantity of nitric acid does not decompose it in the course of twelve hours. In contact with the greater number of heavy metallic oxides dissolved in acids, it forms water and a metallic selenide, the latter compound separating in the form of a brown or black precipitate. With the salts of cerium, manganese and zinc, aqueous hydroselenic acid gives flesh-coloured precipitates of hydrated metallic selenide, or hydroseleniate of metallic oxide. (Berzelius.)

b. With Salifiable Bases. *Hydroseleniates.* (Vid. *Metallic Selenides.*)

Selenium and Phosphorus.

Selenide of Phosphorus. The two bodies are miscible in all proportions at temperatures near the melting point of phosphorus. Phosphorus combined with a large quantity of selenium forms a dark-brown, shining, easily fusible mass, of conchoidal fracture. When a compound containing

excess of phosphorus is distilled, the phosphorus is evolved, together with a small quantity of selenium, in red, translucent drops, which when cold exhibit a brownish-yellow colour and crystalline texture. To warm water, selenide of phosphorus imparts a small quantity of hydroselenic acid; in heated solution of potash it dissolves, forming selenide of potassium or hydroseleniate of potassa, and phosphate of potassa. (Berzelius.)

Selenium and Sulphur.

A. Selenide of Sulphur. Sulphur and selenium may be fused together in all proportions.—*a.* S^2Se is obtained, on passing hydrosulphuric acid gas into aqueous hydroselenic acid, in the form of a precipitate which is first lemon-yellow and afterwards orange-yellow,—remains for a long time suspended in the liquid—is deposited more readily on the addition of hydrochloric acid—collects together, when the liquid is heated, in the form of a fiery-red mass—and exhibits a red colour when dry. It softens at 100° and melts at a few degrees above; at a still higher temperature it boils and distils over, forming when cold a transparent orange-yellow substance like orpiment. When it is burnt in the air sulphurous acid is the chief product at first; afterwards selenic oxide is formed; if the supply of air is but limited, part of the selenium sublimes unburnt. Nitric acid decomposes selenide of sulphur but slowly; aqua regia, easily. A residue is left, consisting of sulphur spotted with red, which obstinately retains a portion of the selenium, and can only be freed from it by fusion in the concentrated acid liquid; it then acquires a pure yellow colour. (Berzelius.) Chlorine gas passed over diselenide of sulphur converts it into a mixture of bichloride of selenium and chloride of sulphur; the latter is easily volatilized by heat, and pure chloride of selenium is left behind. (H. Rose.) Diselenide of sulphur fused with a small quantity of carbonate of potassa forms a mass, which, when digested in water, leaves a residue of selenium; with a larger quantity of carbonate of potassa, a perfectly soluble compound is obtained. A small quantity of cold solution of potash abstracts sulphur from the diselenide, and leaves selenium containing a smaller quantity of sulphur; a large quantity of the potash solution dissolves out the whole of the sulphur together with a portion of the selenium, and leaves pure selenium. Aqueous solution of monosulphide of potassium (simple hydrosulphate of potassa) abstracts sulphur from this compound, forming pentasulphide of potassium (hydrosulphite of potassa) and separating selenium; the same effect is produced by the double sulphide of hydrogen and potassium (bihydrosulphate of potassa), but only after longer boiling. If the liquid is in excess, it also dissolves a portion of selenium and leaves selenium free from sulphur; if its quantity is small, it does not dissolve any selenium. (Berzelius.)

¶ *á.* Triselenide of sulphur, S^3Se, is obtained by fusing together one atom of selenium and 3 atoms of sulphur. In the fused state it is black, much less volatile than sulphur, and may be distilled without alteration. When cold, it is perfectly transparent and of a yellowish red colour. It remains for some time soft and elastic like plastic sulphur, but is not glutinous like the latter. After complete solidification, it becomes opaque and of a brick-red colour. It is perfectly soluble in excess of caustic alkali: if the alkali is not in excess, a portion of the selenium remains behind, and the alkali is converted into a metallic polysulphide. (Berzelius.) ¶

b. A mixture of 100 parts of selenium and 1 part of sulphur is some-

what more fusible, redder, and more transparent than pure selenium. When heated above its melting point, it becomes viscid, black, and opaque, but after cooling down a few degrees, it again acquires greater mobility, and becomes dark-red and translucent.—*c.* 100 parts of sulphur acquire a dirty orange-yellow colour by fusion with 1 part of selenium. (Berzelius.)

B. SELENIUM IN OIL OF VITRIOL. Selenium dissolves rapidly and in large quantities in fuming oil of vitriol, at slightly elevated temperatures. (Magnus.) It does not combine with anhydrous sulphuric acid (Fischer, *Pogg.* 16, 121). When the clear, beautiful green solution in fuming oil of vitriol is mixed with water, it immediately deposits the selenium in the form of a red powder. Only about $\frac{1}{10}$ of the whole quantity of selenium remains in solution, probably oxidated by contact of air and converted into selenious acid; it may be precipitated by sulphuretted hydrogen. (Magnus, *Pogg.* 10, 491; 14, 328.) According to Magnus, the selenium dissolves in the oil of vitriol without alteration. According to Fischer (*Pogg.* 12, 153) it is first oxidated, inasmuch as sulphurous acid is formed in the process of solution, and, on the addition of water, this acid and the oxidated selenium are reconverted into sulphuric acid and free selenium. Oil of vitriol containing anhydrous acid, dissolves selenium at ordinary temperatures; common oil of vitriol dissolves it after boiling for a little while. The former solution, when precipitated by water, gives a filtrate which is scarcely rendered turbid by sulphuretted hydrogen: the latter gives a filtrate rich in selenious acid. Both solutions are dark-green, become yellow on boiling, then suddenly colourless, and no longer give precipitates when mixed with water: they give, however, an orange-yellow precipitate with sulphuretted hydrogen, because the selenium which they contain is in the state of selenious acid. (Gm.)

OTHER COMPOUNDS OF SELENIUM.

A. With Bromine.—B. With Chlorine.

C. With Metals. *Metallic Selenides* or *Seleniurets.* These compounds are obtained in the dry state: 1. By directly fusing the metal with selenium, the combination being often attended with development of light and heat, not so vivid, however, as in the combination of sulphur with the same metals.—2. By precipitating most of the heavy metallic oxides dissolved in acids by means of hydroselenic acid, or of a dissolved selenide of an alkali-metal (alkaline hydroseleniate), or by heating a hydrated metallic selenide (hydroseleniate of metallic oxide). —3. By heating selenium with metallic oxides or their carbonates, whereby part of the selenium is converted into selenious acid. Thus, the alkalis fused with selenium produce an alkaline selenite and a metallic selenide. (Berzelius, *Schw.* 34, 79.)—4. By igniting selenites or seleniates with hydrogen or charcoal.—The metallic selenides are analogous to the sulphides. The selenides of the alkali-metals are red, or, if they contain excess of selenium, dark red-brown, and have the taste and smell of the sulphides of the alkali-metals. The other metallic selenides are mostly dark coloured, and exhibit the metallic lustre: they are generally more fusible than the metals which they contain. When they are heated to redness in the air, the selenium burns slowly with a reddish blue flame, and an odour of horse-radish. Selenium is, however, more difficult to drive off by roasting than sulphur. The selenides are less

easily soluble in nitric acid than the pure metals; selenide of mercury, almost insoluble. Chlorine, with the aid of heat, converts them into chloride of selenium and metallic chloride.

Compounds of Metallic Selenides with Water, which may be regarded as Salts of Hydroselenic acid, Hydroseleniates. These compounds are obtained: 1. By bringing certain metallic selenides in contact with water. Only a few selenides, as those of potassium and sodium, are soluble in water.—2. By passing hydroselenic acid gas through water in which the base is dissolved or diffused: *e. g.* the alkalis and magnesia. On complete saturation with hydroselenic acid, aqueous *Double Selenides of Hydrogen and the Metals*, or *Bi-hydroseleniates*, or Berzelius's *Selenhydrates* are formed.—3. By precipitating the salts of baryta, strontia, lime, the earths, oxide of zinc, or protoxide of manganese, by aqueous hydroseleniate of potassa.—4. By boiling selenium with the aqueous solution of an alkali. In this case, a dark brown solution is produced which, together with an alkaline selenite, contains a metallic poly-selenide or an alkaline hydroselenite.

The hydroseleniates of ammonia, potassa, and soda, are probably colourless when quite pure, but generally have a red tinge, arising from excess of selenium. In taste and smell they resemble the alkaline hydrosulphates; in the state of aqueous solution they impart to the skin a permanent stain of yellow, brown, or black, according to the degree of concentration. When exposed to the air, they are converted into caustic alkali or alkaline carbonate, a metallic-shining film, crystalline on the lower surface, being at the same time deposited; with acids they evolve seleniuretted hydrogen. The mono-hydroseleniates of baryta, strontia, lime, and magnesia are flesh-coloured, and do not dissolve in water unless excess of hydroselenic acid is present, in which case they dissolve as double selenides of the metal and hydrogen, or as bi-hydroseleniates, and then exhibit similar relations. The compounds of hydroselenic acid with other earths, and likewise those with protoxide of manganese and oxide of zinc obtained according to (4), are flesh-coloured precipitates insoluble in water. (Berzelius.) All these precipitates appear to derive their flesh-colour from excess of selenium; for, according to Berzelius, they deposit selenium when decomposed by acids.

CHAPTER VIII.

IODINE.

Memoirs relating to the Sources of Iodine, alphabetically arranged:

Angelini. *Schw.* 36, 319; also *Gilb.* 73, 333.—Aschoff. *Br. Arch.* 20, 148.—Balard. *Ann. Chim. Phys.* 28, 178; also *Schw.* 44, 350; also *Kastn. Arch.* 5, 126.—Bernhardy. *N. Br. Arch.* 26, 199.—Berzelius. *Schw.* 44, 128; *Pogg.* 4, 269.—*Lehrb.* 1, 255.—Bonjean. *J. Chim. Med.* 14, 123.—Boussingault. *Ann. Chim. Phys.* 30, 91; also *Schw.* 46, 113.—*Ann. Chim. Phys.* 54, 163.—Brandes. *Br. Arch.* 16, 107.—*N. Br. Arch.* 13, 156; 15, 157.—Bussy. *J. Pharm.* 25, 718; also *J. pr. Chem.* 19, 495.—Bustamente. *Ann. Chim. Phys.* 62, 110.—Cantu. *Mem. de Turin.* 29, 221; also *Schw.* 44, 351;

also *Kastn. Arch.* 5, 127.—Chevallier. *J. Pharm.* 8, 409.—Creuzburg. *Kastn. Arch.* 27, 221.—Dickie. *Ann. Pharm.* 34, 240.—Egidi. *Brugn. Giorn.* 18, 240; also *Schw.* 45, 128.—Emmet. *Sill. Amer. J.* 18, 260.—Fuchs. *Repert.* 14, 276.—Fyfe. *Ed. Phil. J.* 1, 254; also *Gilb.* 66, 241.—Gaultier de Claubry. *Ann. Chim. Phys.* 13, 298; also *N. Tr.* 5, 1, 371.—Girardin. *Compt. Rend.* 14, 618.—L. Gmelin. *Ann. Pharm.* 31, 321.—Göbel. *Repert.* 11, 44.—Gräger. *N. Br. Arch.* 26, 60 and 187.—Happ. *N. Tr.* 6, 1, 304.—Hausmann. *Ann. Pharm.* 22, 170.—Hayes. *Berzel. Jahrb.* 21, 2, 217.—Von Holger. *Zeitschr. Phys. Math.* 9, 75.—Hall. *N. Tr.* 7, 2, 137; 12, 1, 297.—Hopfer de l'Orme. *Ann. Pharm.* 21, 73.—John. *Schw.* 45, 128; *Kastn. Arch.* 4, 323.—Jonas. *Ann. Pharm.* 26, 346.—Krüger. *Schw.* 32, 292; 37, 444; *Br. Arch.* 11, 383.—Liebig. *Kastn. Arch.* 5, 454.—*Mag. Pharm.* 16, 124.—Marchand. *J. pr. Chem.* 19, 151.—Meissner. *Schw.* 43, 68.—Menzel & Cochler. *Kastn. Arch.* 12, 252; 13, 336; *Schw.* 50, 252.—Morin. *J. Pharm.* 27, 84.—Meyer. *N. Tr.* 5, 2, 430.—Nentwich & Pleischl. *Zeitschr. Phys. Math.* 4, 91 and 97.—Pfaff & Van der Smissen. *Schw.* 45, 378.—Preuss. *Ann. Pharm.* 34, 229.—Ragazzini. *J. Chim. Med.* 11, 360.—Del Rio. *Schw.* 50, 494; 51, 253.—*Ann. Chim. Phys.* 62, 110; abstr. *Pogg.* 39, 526.—Sarphati. *Repert.* 59, 314.—Sgarzi. *J. Chim. Med.* 10, 738.—Steinberg. *J. pr. Chem.* 25, 387.—Stoltze. *Berl. Jahrb.* 29, 1, 202.—Straub. *Schweiz. Naturw. Anzeiger. Jahrg.* 3, 59; also *Gilb.* 66, 249.—Stratingh. *Repert.* 15, 282.—Torosiewicz. *Repert.* 34, 8; 36, 169; 61, 395; 63, 114; 66, 314.—Turner. *N. Ed. Phil. J.* 1, 159.—Vauquelin. *Ann. Chim. Phys.* 29, 410; also *N. Tr.* 11, 1, 25.—A. Vogel. *Kastn. Arch.* 6, 333.—Wackenroder. *N. Br. Arch.* 15, 197; 17, 187; 24, 140; 26, 321.—Waltl. *Repert.* 66, 314.—Yniestra. *Ann. Chim. Phys.* 62, 111; also *Pogg.* 39, 526.

Iodine in general:

Courtois, Clement & Desormes. *Ann. Chim.* 88, 304; also *Gilb.* 48, 367. Sir H. Davy. *J. Phys.* 77, 456; also *Gilb.* 48, 32.—Further: *Phil. Trans.* 1814, I., 74; *Schw.* 11, 68; also *Gilb.* 48, 19.—Further: *Phil. Trans.* 1814, II., 487; *Schw.* 11, 234.—Further: *Ann. Chim.* 92, 89.—Further: *Schw.* 16, 343; also *Ann. Chim.* 96, 289.

Vauquelin. *Ann. Chim.* 90, 239; also *Schw.* 13, 394; 14, 44; also *Gilb.* 48, 305.

Gay-Lussac. *Ann. Chim.* 88, 311; also *Gilb.* 48, 24.—Further: *Ann. Chim.* 88, 319; also *Gilb.* 48, 372.—Further: *Ann. Chim.* 91, 5; also *Schw.* 13, 384; also *Gilb.* 49, 1 and 211.

Colin. *Gilb.* 48, 280.

Colin & Gaultier de Claubry. *Ann. Chim.* 90, 87; also *Gilb.* 48, 297; also *Schw.* 13, 453.

Inglis. *Phil. Mag. J.* 7, 441; 8, 12 & 191; also *J. pr. Chem.* 7, 394.

Preparation of Iodine:

Accum, Fisher, Garden. *Gilb.* 48, 5 and 18. Thomson, Wollaston. *Gilb.* 48, 277. Soubeiran. *J. Pharm.* 13, 421? also *Pogg.* 12, 604; also *N. Tr.* 16, 2, 132.—Whytelaw. *Pogg.* 39, 199.—Bussy. *J. Pharm.* 23, 17; also *Ann. Pharm.* 22, 62; also *J. pr. Chem.* 13, 251.—Mohr. *Ann. Pharm.* 22, 66.—Graham. *Elements, New Ed.* pp. 492, 493.

Iodic Oxide and *Iodous Acid*:

Sementini. *Bibl. univ.* 25, 119; also *Schw.* 41, 158;—*Brugn. Giorn.* 19, 387; also *Schw.* 49, 103;—*Phil. Mag. J.* 4, 392; also *J. Pharm.* 21, 254; *J. of Roy. Inst.* 2, 75; abstr. *Schw.* 65, 453.
Pleischl. *Kastn. Arch.* 6, 155; also *Schw.* 45, 1.
Wöhler. *Pogg.* 8, 95.
Mitscherlich. *Pogg.* 11, 162; 17, 481.
Inglis. *Phil. Mag. J.* 7, 442.

Iodic and *Hyperiodic Acid*:

Serullas. *Ann. Chim. Phys.* 43, 113, 208, 211, 216; 45, 59; also *Pogg.* 18, 97 and 112; 20, 515.
A. Connell. *N. Ed. Phil. J.* 10, 93 and 337, 11, 72; also *Schw.* 62, 493. *N. Ed. Phil. J.* 13, 284.
Rammelsberg. Iodates. *Pogg.* 44, 545.
Magnus & Ammermüller. Hyperiodic Acid. *Pogg.* 28, 514.
Benckiser. *Ann. Pharm.* 17, 254.
Millon. Iodic Acid. *N. Ann. Chim. Phys.* 19, 400.

Metallic Iodides:

P. Boullay. *Ann. Chim. Phys.* 34, 337; also *Schw.* 50, 362; *N. Tr.* 16, 1, 122; abstr. *Pogg.* 11, 99.
Berthemot. *J. Pharm.* 14, 610; also *N. Tr.* 18, 2, 113.

Iod, Iode, Varec, Iodum, Iodina. From τὸ ἴον, the Violet.

History. Discovered in 1812 by M. Courtois, a manufacturer of saltpetre; very minutely examined by Gay-Lussac in 1813—1814.

Sources. As iodide of mercury (Del Rio); as iodide of silver. (Vauquelin; Del Rio.) In the white lead ore of Catorce in Mexico. (Bustamente.) In very small quantities, in the zinc ore of Silesia. (Menzel & Cochler.) Sublimes as hydriodate of ammonia mixed with sal-ammoniac in the burning coal-mine of Commentry. (Bussy.) As iodide of potassium or sodium in nitrate of soda from Chili. (Hayes; Lembert.) In the rock-salt of Hall in the Tyrol, probably in the form of iodide of sodium. (Fuchs.)

In the following salt-springs, probably as iodide of sodium, calcium or magnesium: Bex (Morin); Sülze in Mecklenburg (Krüger); Kolberg in Pomerania (John); Salzuffeln and Königsbronn near Unna (Brandes); Rehme near Minden (Aschoff); Schönebeck (Hermann; Steinberg); Halle in Saxony (Meissner); Dürrenberg and Kösen (Stoltze); Artern and Salzungen (Wackenroder); Schonalkalden (Bernhardy); Salzhausen and Kreuznach (Liebig); Bolechow and Drochobycz in Gallicia (Torosiewiez); Kenahwa in North America (Emmet); Guaca in the province of Antioquia in New Granada. (Boussingault.)

In the following other mineral waters:—A well at Saragossa (Sgarzi); the thermal springs of Albano (Raggazini); spring near Sales in Piedmont (Angelini); several saline springs near Ascoli (Egidi); hepatic water of Castel Nuovo d' Asti (Cantu); thermal spring of Aix in Savoy, called

"*Source de soufre*," (Bonjean); Bonnington water, near Leith (Turner); Bath water (Br. Arch. 38, 184); Marienbad in Bohemia, containing but very little iodine (Berzelius); Carlsbad (Creuzburg and Nenntwich & Pleischl); Heilbrunn in Bavaria, rich in iodine (A. Vogel); spring at Künzig, in Bavaria (Waltl); medicinal water (*Kropfwasser*) of Hall in Austria, used for the cure of goitre, (Von Holger); hepatic water of Trutkawiec, and alkaline water of Iwonicz in Gallicia (Torosiewicz).

The quantity of iodine contained in sea-water is so small, that Tennant, Sir H. Davy, Gaultier, Fyfe, and Sarphati were not able to find it. Balard however found it in the water of the Mediterranean, and Pfaff in that of the Baltic, which nevertheless is very poor in iodine. But plants and animals which live in the sea appropriate the iodine in large quantities, in the form of iodide of potassium, sodium, calcium, or magnesium; and these salts may be extracted from the plants by water, either before, or more completely after incineration.

Marine and littoral plants in which iodine is found:—(the bracketted numbers denote the quantity of iodine in 100 parts of the dry plant, as determined by Sarphati):—*Fucus Filum* (0·0894), *digitatus* (0·135), *saccharinus* (0·23), *nodosus* (contains but little iodine), *vesiculosus* (0·001), *saccatus* (0·124), *Lorcus* (very little) *siliquosus* (0·142). The following plants, according to Davy, Gaultier, and Fyfe, also contain iodine: *Fucus cartilagineus*, *membranaceus*, *rubens*, and *palmatus*. *Sphærococcus* (*Ceramium*) *Helmintochortos*, according to Straub, Happ and Gaultier; and *Sphaerococcus crispus*, according to Sarphati. *Ulva Linza*, *pavonia*, *umbilicalis* (0·059), H. Davy, Sarphati; and *Lactuca* (0·055), Sarphati. *Zostera marina* (0·0005), Balard, Sarphati. *Lichen confinis*, *Statice armeria*, and *Grimmia maritima*, growing upon rocks on which sea-water is sometimes blown by the wind; but *Ramelina scopulorum*, growing in the same situation, contains no iodine. (Dickie.) The following, though they grow near the sea, contain no iodine. *Salsola Kali:* (Fyfe, Sarphati, Dickie.) *Plantago maritima* (Fyfe, Sarphati), and *Nicotiana Tabacum* (Sarphati). *Pilæ marinæ* contain iodine (Meyer). The ashes of various species of *Fucus*, *Ulva*, and other sea plants, which constitute the *Varec* of Bretagne and *Kelp* of Scotland, are rich in iodine (Courtois, Fyfe); the ashes of different kinds of *Salsola* and other shore-plants, *e. g.* the Spanish *Barilla* and the Roman and Sicilian *Soda*, contain little or no iodine. (H. Davy; Fyfe.)

Marine animals containing iodine: Common Sponge (Gaultier, Fyfe, Straub, Göbel, Stratingh); Horse-sponge (Stratingh); *Lapis spongiarum* (Happ). *Spongia oculata* (Sarphati); *Flustra foliacea*, various species of *Sertularia* and *Tubularia* (poor in iodine), Sarphati; various kinds of *Rhizostoma* and *Cyana* (rich in iodine), Sarphati; *Asterias rubens*, *Crognon vulgare*, *Mytilus edulis* (containing a small quantity of iodine, but much more bromine), Sarphati;—Oysters, various species of *Doris* and *Venus* (Balard). *Pleuronectes Flesus* (containing a little iodine, but much richer in bromine), Sarphati;—*Cod liver oil* (*Berger Leberthran;* the oil from the liver of *Gadus Morrhua* and other species of Gadus) contains iodine (Hopfer de l'Orme, Hausmann, Brandes, Wackenroder, Gräger, Marchand, L. Gemelin); 100 parts of the light-brown oil contain, according to Gräger, 0·0846, and according to Wackenroder, from 0·162 to 0·324 parts of iodine. The oil from the liver of *Raja clavata* and *R. Balis* also contains iodine. (Girardin.) Salted Scotch herrings contain a trace. (Jonas.) No iodine could be detected in corals (Fyfe, Stratingh); in the eggs of *Buccinum undatum* (Sarphati); or in isinglass (Stratingh.)

Plants and animals living at a distance from the sea, but containing iodine: A species of *Salsola* (*los Romeritos*), which grows in the floating gardens on the fresh-water lakes near the city of Mexico; a kind of *Agave*, growing in the plains and on the mountains near Mexico. (Yniestra.) Turf from the neighbourhood of Hofwyl. (Straub.) The yellow juice which exudes from *Julus fœtidissimus* when touched; this juice gives a blue colour with starch. (Holl.)

Preparation. Varec or Kelp, the ashes of various species of Fucus and Ulva, is exhausted with hot water; the solution freed as much as possible by evaporation and cooling, from the crystallized salts contained in it (chloride of potassium, chloride of sodium, carbonate of soda, sulphate of soda, &c.); and the mother-liquor—which, besides iodide of sodium, still contains sulphide of sodium, hyposulphite of soda, and a portion of the salts already mentioned*—is subjected to one of the following processes: 1. It is heated in a subliming apparatus with oil of vitriol. (*Sch.* 91):

$$NaI + 2SO^3 = NaO, SO^3 + SO^2 + I.$$

This method is not very advantageous; because the sulphurous acid evolved acts upon the iodine and the water which is present, in such a manner as to produce hydriodic and sulphuric acid. (Soubeiran.)

2. The mother-liquor is heated in a subliming apparatus with peroxide of manganese and oil of vitriol. (Wollaston, *Sch.* 67.)

$$NaI + 2SO^3 + MnO^2 = NaO, SO^3 + MnO, SO^3 + I.$$

A. Whytelaw adds one measure of oil of vitriol, carefully and in small portions at a time, to eight measures of the mother-liquor, contained in a leaden boiler—whereupon, carbonic acid and sulphuretted hydrogen (from the sulphide of sodium) are first evolved; and, after exposure to the air for a day or two, sulphurous acid (from the hyposulphite of soda) escapes, and sulphur is precipitated. He then pours off the liquid from the crystallized sulphate of soda into a leaden cylinder placed horizontally in a sand-bath, and fitted with a helm, the beak of which passes into the first of three tubulated receivers luted one into the other; heats the mixture to 65° (149° F.); and, after adding the peroxide of manganese and putting on the helm, gradually raises the temperature to 100°, but not higher, because at 118° (244° F.) chloride of iodine begins to distil over. Sometimes also, cyanide of iodine collects in the last receiver, in white, needle-shaped crystals. The liquid which remains in the retort still contains iodine, and on cooling, deposits crystals of iodide of lead and double iodide of lead and sodium.

3. The mother-liquor is evaporated to dryness, the residue heated with peroxide of manganese, and the iodine precipitated from the filtered solution by chlorine. *Barruel's method:* The residue obtained by evaporating the mother-liquor to dryness is mixed with $\frac{1}{10}$ of its weight of peroxide of manganese, and the mixture heated in an iron vessel to commencing redness (stirring all the while), but not high enough to cause the evolution of vapours of iodine: the heat is continued till a sample of the mixture treated with sulphuric acid no longer evolves sulphuretted hydrogen or deposits sulphur; that is to say, till the whole of the sulphide of sodium and hyposulphite of soda are converted into sulphate.

* A mother-liquor from Varec examined by Soubeiran contained no carbonate or sulphate: the principal salts contained in it—in addition to the iodides—were nitrate of lime and nitrate of magnesia.

The mass is then dissolved in such a quantity of water that the solution may have a density corresponding to 36° of Baume's areometer; chlorine gas is passed through the filtered liquid, which is constantly stirred, till a sample treated with more chlorine no longer gives a precipitate of iodine (excess of chlorine would convert the iodine into chloride and re-dissolve it), and the pulverulent precipitate of iodine is collected on a filter, and purified by sublimation. (Bussy.) Mohr is of opinion that a loss of iodine may occur in this process during the heating of the evaporated residue with manganese.

4. The mother-liquor is precipitated by a copper-salt and metallic iron, and the diniodide of copper heated with peroxide of manganese. *Soubeiran's method:* The mother-liquor is diluted with water, and mixed with a solution of sulphate of copper, as long as any precipitate is produced:

$$2NaI + 2(CuO, SO^3) = 2(NaO, SO^3) + Cu^2I + I;$$

the liquid containing the free iodine separated by decantation and washing from the precipitated diniodide of copper, and mixed with sulphate of copper and iron filings till it no longer smells of iodine:

$$I + 2\,(CuO, SO^3) + 2Fe = Cu^2\,I + 2(FeO, SO^3);$$

and the diniodide of copper thus produced, quickly separated by elutriation from the excess of iron filings and from the liquid, before the ferrous sulphate has time to oxidate in the air. The two portions of diniodide of copper obtained as above, are next dried at a gentle heat (a stronger heat would decompose the diniodide of copper—since it is mixed with disulphate of ferric oxide—and evolve iodine); the whole mixed with twice or three times its weight of peroxide of manganese, and a sufficient quantity of oil of vitriol to form it into a paste; and the mixture strongly heated in a subliming apparatus:

$$Cu^2I + 2MnO^2 + 4SO^3 = 2(CuO, SO^3) + 2(MnO, SO^3) + I.$$

Or the oil of vitriol is dispensed with, and a stronger heat applied:

$$Cu^2I + 3MnO^2 = 2CuO + Mn^3O^4 + I.$$

In both cases, the iodine which passes over is accompanied by water derived from the hydrated diniodide of copper, from the sulphate of lime precipitated with it, and from the oil of vitriol, when it is used in the process. In this water, a portion of the iodine is dissolved: it may be again precipitated by sulphate of copper. By this process, 100 parts of the mother-liquor yield 1 part of iodine.

Purification. The iodine obtained by the preceding processes is purified by washing with a small quantity of water, pressing between paper, drying, and subliming a second time. The iodine of commerce may be completely purified by solution in alcohol, filtering, and precipitating with water. (Serullas.)

Properties. The crystalline system to which iodine belongs is the right prismatic. Primary form: an acute rhombic octohedron (*Fig.* 41, 42, 43, 46; also 43, with *m*-faces). Ratio of the 3 axes = 4 : 3 : 2. (Wollaston, Marchand, *Pogg.* 31, 540; Lampadius & Breithaupt, *J. pr. Chem.* 13, 237);—*compare* Plisson (*Ann. Chem. Phys.* 39, 274), Soubeiran (*J. Pharm.* 13, 423). The finest crystals are obtained from solutions; *e. g.* from aqueous hydriodic acid exposed to the air, or from a solution of

iodine in ether. Iodine yields by sublimation, laminæ or broad oblique tables formed by extension of the *p*-surface (according to Plisson and Soubeiran, acute rhombohedrons and double six-sided pyramids). Specific gravity = 4·948 at 17°. (Gay-Lussac.) Very soft and friable; may be reduced to powder. Blackish-grey, with metallic lustre, resembling black-lead or micaceous iron ore; transmits light only when in thin pieces; the transmitted light is red. Fuses at 107° (224·6° F.), and on cooling solidifies again in a lamellated mass. Boils (under oil of vitriol) between 175° and 180° (347°—356° F.), according to Gay-Lussac, and is converted into a violet vapour which deposits crystallized iodine on colder bodies. The saturated vapour is so dark coloured that a stratum 4 inches thick is impervious to daylight or candlelight: it appears blue on the edges, and by reflected light perfectly black. (Dumas.) Specific gravity of the vapour (I., 279). Solid iodine is a non-conductor of electricity. (Gay-Lussac; Solly, *Phil. Mag. J.* 8, 130; also *Pogg.* 37, 420; Inglis.) Fused iodine conducts the current of a battery containing from 60 to 90 pairs. (Inglis, Knox, *Phil. Mag. J.* 9, 450; 16, 188.) The odour of iodine resembles that of chlorine, chloride of sulphur, or oxide of osmium; its taste is sharp and astringent; it acts as a powerful poison. It exerts but a feeble action on vegetable colours. Pulverized iodine and the saturated aqueous solution decolorize tincture of litmus and infusion of red cabbage, in the course of a few days. (A. Connell, *N. Ed. Phil. J.* 12, 337; also *Ann. Pharm.* 3, 314.) Iodine communicates a transient brown colour to the skin and to paper, due to the formation of hydriodous acid. It produces a bright blue colour with starch and meconine. With bisulphide of carbon and rock-oil it forms bright, violet-coloured solutions.

Atomic weight of iodine: 124 Prout; Thomson; 125 Gay-Lussac; 126·56 (the double atom) Berzelius.

Compounds of Iodine.

Iodine and Water.

One part of iodine dissolves in 7000 parts of water (Gay-Lussac); in 500 parts at 20° (Jacquelain, *Ann. Chim. Phys.* 73, 201), forming a brown solution, which has the smell of iodine. The solution loses its colour by exposure to the direct rays of the sun (Ampère); also in perfectly closed bottles, provided they contain air, but not if they are completely filled with the liquid. (Inglis.) The decolorized solution, when brought in contact with iodine, dissolves it, and acquires a permanent orange-yellow tint. (Guibourt, *J. Chim. Méd.* 5, 103.) From this it would appear that the decolorized liquid contains hydriodic acid, which, by taking up an additional quantity of iodine, is converted into hydriodous acid. (Gm.)

Iodine and Oxygen.

A. Iodic Oxide?

Oxide of Iodine.

1. Oxygen gas is passed through a bent copper tube kept at a low red heat, into the tubulure of an empty retort, heated by a spirit-lamp; and a spoon filled with iodine is introduced through the neck of the retort, in such a manner, that the stream of heated oxygen may come

into immediate contact with the iodine. The iodine, as it volatilizes, is converted into amber-coloured vapours, which condense in the neck of the retort, forming a transparent mass, nearly solid at first, but afterwards becoming oily.—2. An intimate mixture of peroxide of barium and excess of iodine is heated over the flame of a spirit-lamp. Violet vapours of iodine pass over at first; afterwards, yellow vapours of iodic oxide. With baryta and iodine the product is smaller; oxygen is evolved in both cases.

Iodic oxide is a thick, brownish-yellow, oily liquid; perfectly volatile; smelling of iodous acid; of harsh, disagreeable taste; and turning litmus paper green (from mixture of the blue colour of the litmus, with the yellow of the iodic oxide. *Gm.*). It sets fire to phosphorus and potassium at ordinary temperatures; deposits a black film of iodine on paper, which takes up its oxygen; and forms coloured solutions with water and alcohol. Its aqueous solution is instantly decolorized by potash, without precipitation of iodine. (Sementini.)

On passing *dry* oxygen gas through a tube heated not quite to redness, and containing iodine at the end where the oxygen entered, so that the mixture of iodine vapour and oxygen gas was made to traverse the hot part of the tube, the author obtained nothing but sublimed iodine—no iodic oxide.

B. Iodous Acid?

a. An intimate mixture of 1 part of iodine, and from 1 to 3 parts of chlorate of potassa, is distilled by the heat of a spirit-lamp. At first, a small quantity of free iodine may be evolved; then follows yellowish vapour of iodic oxide, which does not redden litmus paper; then iodous acid, which condenses to a thick oily liquid. If the heat be still further continued, iodic acid enters into combination with the potassa, and disengages chlorine, which contaminates the last portions of iodous acid. Or better: Chlorate of potassa is heated in a tubulated retort till it has lost all its moisture, and a spoon filled with iodine introduced through the tubulure, and sunk nearly to the bottom of the retort. The vapour of iodine, which is at first evolved of a violet colour, brings the chlorate of potassa into a state of violent commotion; whereupon, yellow vapours of iodous acid are given off, and condense in the neck of the retort. The iodous acid thus produced is an amber-coloured liquid, of a thick, oily consistence, specifically lighter than water (?). It evaporates completely in the air, rapidly at 50°, producing yellow vapours; reddens litmus without bleaching it; tastes slightly acid, but harsh and burning. It is decomposed by potassium or phosphorus, with evolution of light and heat; the decomposition by phosphorus is moreover attended with production of violet vapours. It dissolves in water or alcohol, forming a yellow solution. Sulphurous acid precipitates iodine from its aqueous solution; potassa converts it into iodate of potassa, with separation of iodine. (Sementini.) Pleischl obtained similar results. On the other hand, Wöhler showed that when iodine is distilled with chlorate of potassa, the only product is chloride of iodine, which is brown and liquid when a large quantity of iodine is employed, yellow and solid when the quantity of iodine is small. Hence it would appear that the iodous acid obtained as above, is in reality chloride of iodine; and it must be observed that Sementini has not demonstrated either the presence of oxygen in it or the absence of chlorine.

b. 3 parts of iodic oxide concentrated as much as possible, are added to an aqueous solution of 100 parts of iodic acid: a larger quantity of the oxide causes precipitation of iodine, and decolorization of the liquid. [This effect is easily explained, if we suppose Sementini's iodous acid to be really hydriodous acid. *Gm.*] The product is an amber-coloured liquid [aqueous iodic acid, containing a small quantity of iodine in solution], which loses its yellow colour by exposure to the air, in consequence of the volatilization of the iodic oxide [iodine]. (Sementini.)

c. When bibasic periodate of soda ($2NaO, IO^7$) is gently ignited, it gives up only 6 atoms of oxygen (by strong ignition, 8 atoms are driven off, and there remains NaO, NaI). The residue may be regarded either as $2NaO, IO$, or $NaI, 3NaO, IO^3$: according to the first view, it contains a hypo-iodous acid, IO; according to the second, an iodous acid, IO^3. The aqueous solution of this residue turns reddened litmus blue at first, and bleaches it gradually afterwards. By boiling, it loses its bleaching power, and is converted into iodate of soda. These relations are analogous to those of the bleaching compounds of chlorine, in which Balard demonstrated the existence of hyperchlorous acid, ClO. (Magnus & Ammermüller.) The following older observations likewise relate to this matter: baryta, strontia, or lime at a red heat, takes up iodine without evolving oxygen. The solution of these compounds in water has a strong alkaline reaction. (Gay-Lussac.) The same compounds when strongly ignited, give up their iodine. (Grouvelle.) Magnesia in contact with iodine and water forms but little iodide of magnesium (hydriodate of magnesia), and iodate of magnesia, but is, for the most part, converted into a brown powder, which may be regarded as iodide of magnesia [or perhaps as hypo-iodite of magnesia, *Gm.*]. This powder, when heated alone, is resolved into vapour of iodine and magnesia, and when heated in contact with water, into iodide of magnesium (hydriodate of magnesia), and iodate of magnesia. (Gay-Lussac.)

d. When iodine is added to a solution of caustic soda (not too highly concentrated), till the liquid begins to exhibit a permanent colour, and the solution left to evaporate at a low temperature, crystals are obtained, the composition of which may be expressed either by the formula: $NaI + NaO, IO^5 + 20Aq.$, or by; $NaO, IO^2 + 10Aq.$ According to the latter view, they consist of an iodite of soda, the acid of which has the composition IO^2. The soda compound of this acid is the only one that can be obtained. (Mitscherlich.) Vid. *Sodium.*

C. Iodic Acid. IO^5.

Iodsäure, Iodinesäure, Oxiodinsäure, Acide iodique.

Formation. The affinity between iodine and oxygen is so small, that iodine and oxygen gas will not act upon one another at any temperature. Iodine is not combustible; it can only, under certain circumstances, take up oxygen previously existing in a state of combination with another substance.—1. Iodine, in contact with hypochlorous acid (and its salts), and likewise with chloric oxide (H. Davy), forms iodic acid and chloride of iodine.—2. With concentrated nitric acid, it forms iodic acid and hyponitric acid. (Connell.)—3. Iodine, in contact with excess of chlorine and a large quantity of water, forms hydrochloric and iodic acid:

$$I + 5Cl + HO = 5HCl + IO^5;$$

and if an alkali be present, a metallic chloride and an alkaline iodate are produced (Gay-Lussac);

$$6KO + I + 5Cl = 5KCl + KO, IO^5.$$

4. Iodine and aqueous solution of potassa form 5 atoms of iodide of potassium and 1 atom of iodate of potassa.

$$6KO + 6I = 5KI + KO, IO^5;$$

or, what comes to the same thing, 5 atoms of hydriodate of potassa and 1 atom of iodate of potassa (*Sch.* 33 and 34; for Cl read I):

$$6KO + 6I + 5HO = 5(KO, HI) + KO, IO^5.$$

Similar products are obtained with the other fixed alkalis, and partially also with magnesia. (Gay-Lussac.) In like manner, mercuric oxide, with iodine and water, forms protiodide of mercury and iodate of mercuric oxide (Colin); and oxide of silver with iodine dissolved in alcohol, forms iodide and iodate of silver. (Serullas.)—5. Oxide of gold in contact with iodine and water, forms iodic acid and metallic gold (Colin):

$$3I + 5AuO^3 = 3IO^5 + 5Au.$$

Preparation. Chloric oxide gas is passed over iodine, a gentle heat being applied to volatilize the chloride of iodine formed at the same time. (H. Davy.) Davy passes euchlorine gas (a mixture of chloric oxide and chlorine) obtained by cautiously heating a mixture of 10 grains of chlorate of potassa and 40 grains of hydrochloric acid, sp. gr. 1·105—first over chloride of calcium, for the purpose of drying it, and then over 4 grains of iodine. Instead of hydrochloric acid, Döbereiner (*Schw.* 16, 356) recommends 60 grains of oil of vitriol, which disengages pure chloric oxide. ¶ Millon digests 4 parts of iodine with 7·5 of chlorate of potassa in 40 parts of water acidulated with 10 of nitric acid, heating the liquid sufficiently to cause rapid evolution of chlorine. In a short time the iodine is completely oxidized. The iodic acid thus formed is precipitated by baryta, and separated again by means of sulphuric acid. Larger crystals are obtained when the solution is contaminated with sulphuric acid than when it is pure. (Millon, *N. Ann. Chim. Phys.* 9, 400.) ¶

2. Iodine is oxidated by continued boiling with concentrated nitric acid. (Connell.) The acid must be as strong as possible: the admixture of hyponitric acid recommended by Serullas confers no advantage. To prevent, as far as possible, the volatilization of the iodine in the acid vapours, a flask should be used having a long neck, and a capacity more than 50 times that of the liquid; the lamp must be applied to the bottom only of the flask; the sublimed iodine frequently washed down again, and the heat continued till all the iodine is dissolved: as the liquid cools, the iodic acid separates in a granular mass. The liquid is then evaporated to dryness, twice redissolved in water, and again evaporated. With the removal of the adhering nitric acid, the iodic acid loses its crystalline aspect, and becomes a whitish mass, frequently tinged with red, from separation of iodine. (Connell.)—Boutin (*J. Pharm.* 19, 222) digests 1 part of iodine freshly precipitated by water from an alcoholic solution (because in this state it is purer and more finely divided than ordinary iodine) in a mixture of 8 parts of strong nitric and 2 parts of hyponitric acid. The iodine is first heated with two-thirds of the mixture, in a flask which has a long neck and also a long tube attached to the neck, the liquid being frequently agitated; afterwards, the remaining portion of the mixture is

added; and when the oxidation is complete, the liquid is evaporated to one-third of its bulk: the mother-liquor, when cold, is poured off from the crystallized iodic acid. The latter is then dissolved in a small quantity of water; the filtrate mixed with twice its volume of nitric acid, by which the iodic acid is precipitated; the pale rose-coloured liquid poured off; the precipitated acid dissolved in 3 times its weight of water; 3 measures of the solution mixed with 2 measures of nitric acid; and the mixture evaporated to dryness. Duflos (*Schw.* 62, 496) recommends nitric acid of specific gravity 1·55, and as free as possible from hyponitric acid. Acid of this strength begins to act even in the cold. Acid of specific gravity 1·35 produces no iodic acid even on boiling. Hyponitric acid is hurtful: it decomposes the iodic acid again, and precipitates iodine. Bourson (*Compt. Rend.* 13, 1111; also *J. pr. Chem.* 25, 298) likewise recommends the strongest nitric acid, containing only 1 atom of water; 4 parts of it convert 1 part of iodine, at a gentle heat, almost wholly into iodic acid, very little iodine going off in vapour. The solution with the crystalline grains already produced being evaporated to dryness, the residue exposed to the air till it deliquesces to a syrup, and this syrupy liquid placed for a few days in a hot-air chamber, the acid is obtained in beautiful white crystals.

3. When terchloride of iodine moistened with water is treated with alcohol or ether, decomposition ensues, and iodic acid is left undissolved. (Serullas.) Probably in this manner:

$$2ICl^3 + 5HO = IO^5 + 5HCl + ICl.$$

Hence it would appear that the alcohol takes up hydrochloric acid and monochloride of iodine. Iodine purified by solution in alcohol, filtering, precipitation with water, washing, and drying, is completely saturated with chlorine gas: the terchloride of iodine thus obtained is brought to the state of a soft powder by shaking it up in a bottle with pieces of broken glass and a small quantity of water, and transferred from the bottle into a basin by means of a funnel, whereby the pieces of glass (which should be rinsed with a saturated solution of chloride of iodine) are retained. After pouring off the watery liquid—which may contain monochloride of iodine, and thereby act injuriously—alcohol of 40° B., or ether, is added in successive portions (stirring continually) to the pulverized terchloride of iodine, then decanted and renewed, as long as it acquires a yellow colour. After this, there remains a white crystalline powder of pure iodic acid, which may be obtained in regular crystals by solution in water, filtering, and evaporation in the hot-air chamber, after the addition of sulphuric acid. (Serullas.) The iodic acid thus obtained amounts to only $\frac{1}{7}$ of the quantity of iodine employed. (Liebig, *Pogg.* 24, 363.)

4. Iodine diffused in water is converted by excess of chlorine into iodic acid, and the hydrochloric acid produced at the same time removed by a suitable quantity of oxide of silver. (Serullas; Thompson.)—126 grains (1 At.) of iodine are diffused through 24 oz. of water, and washed chlorine gas passed through the liquid till it becomes colourless. The solution is then freed from excess of chlorine by exposure to the air for an hour, and subsequent heating to 100°; after which it is boiled for ten minutes with freshly precipitated oxide of silver, and lastly filtered and evaporated. (Lew. Thompson.) For the removal of the hydrochloric acid produced in this process, it appears to be necessary to use not merely $2\frac{1}{2}$, but 5 atoms of oxide of silver.

5. **A salt of iodic acid is decomposed by a stronger acid.**—*a.* A solu-

tion of iodate of soda (iodate of potassa will not do, because it gives up only part of its base, and is converted into a ter-iodate) is mixed with excess of hydrofluosilicic acid; the liquid evaporated to a certain point; the acid filtered from precipitated fluoride of silicium and sodium; evaporated, with gentle ebullition and frequent addition of water, till it acquires a syrupy consistence, and no longer smells of fluosilicic acid; then left to cool, and filtered to separate it from an additional quantity of precipitated fluoride of silicium and sodium; and finally dried at a gentle heat, whereby it is rendered perfectly solid. Iodic acid thus prepared yields, when heated, only 1 per cent. of fixed residue. (Serullas.)—*b*. An aqueous solution of iodate of soda is heated for a quarter of an hour with excess of sulphuric acid, to the temperature of commencing ebullition; the filtered liquid placed in a hot-air chamber at 20°—25° (68°—77° F.); the mother-liquor, which contains sulphate of soda, sulphuric acid, and a small quantity of iodic acid, poured off from the crystallized iodic acid; and the latter washed with a very small quantity of water. This process yields a pure acid, which volatilizes without residue. If, however, it should still contain a small quantity of iodate of soda, the process of heating with water and sulphuric acid, and subsequent crystallization, must be repeated till a pure acid is obtained. (Serullas.)—*c*. Iodate of baryta is decomposed by dilute sulphuric acid. (Gay-Lussac.) Liebig (*Pogg.* 24, 362) saturates water, in which iodine is diffused, with chlorine; neutralizes the liquid with carbonate of soda; passes chlorine gas through it till the iodine precipitated by neutralizing the liquid has been redissolved; neutralizes again with carbonate of soda; precipitates the solution thus obtained, which contains chloride of sodium and iodate of soda, with chloride of barium; washes and dries the precipitated iodate of baryta, boils 9 parts of it with 24 parts of water and 2 parts of oil of vitriol for half an hour; and evaporates the filtrate to the consistence of syrup: this liquid, after several days' exposure to the air, yields beautiful crystals of iodic acid. A similar process is adopted by Grosourdy (*J. Chim. Med.* 9, 428). Duflos (*Schw.* 62, 390) finds the use of iodate of baryta more advantageous than that of iodate of soda (5, *a* and 5, *b*).

To obtain the acid in the crystallized state, the syrupy solution is either left to itself in a dry place at ordinary temperatures, and the liquid poured off before the whole is solidified, or it is mixed with hydrofluoric, nitric, or sulphuric acid, and evaporated in the hot-air chamber at a moderate heat. These acids appear to favour crystallization by abstracting water from the iodic acid; moreover, their adhesion to the crystallized acid is merely mechanical, so that the crystals may be entirely freed from them either by pressure between bibulous paper, or, if the acids are volatile, by exposure to warm air. (Serullas.) Rammelsberg also (*Pogg.* 46, 159) found that iodic acid crystallized from a liquid containing sulphuric acid, was free from water and almost wholly free from sulphuric acid.

Properties. Iodic acid crystallizes in six-sided tables which appear to be segments of an octohedron (Serullas). Sinks rapidly in oil of vitriol. (H. Davy.) It is white (sometimes, if it has been too strongly heated, having a pale-red colour, from the presence of free iodine) and translucent. (H. Davy.) Has a very slight odour, peculiar to itself, but resembling that of iodine (Serullas); tastes very sour and disagreeable. (H. Davy.) When dissolved in water, it reddens litmus paper and afterwards bleaches it (H. Davy); reddens it permanently without bleaching it. (Connell.)

Calculation.				Vol.
I	126	75·9	Vapour of iodine	2
5O	40	24·1	Oxygen gas	5
IO^5	166	100·0		

($I^2O^5 = 2 . 789·75 + 5 . 100 = 2079·50$. Berzelius.)

Decompositions. 1. When heated to the boiling point of olive oil, iodic acid fuses, and at the moment of fusion is resolved, without residue, into oxygen gas and vapour of iodine. (H. Davy.)—2. For the decomposition by electricity, *vid.* I., 434, 452.—3. When heated with charcoal, sulphur, resins, sugar, or finely divided combustible metals, it gives up its oxygen to these bodies without detonation. (H. Davy.)—4. The aqueous acid is decomposed by phosphorus, on the application of heat, the products being iodine, phosphoric oxide, and phosphoric acid (Benckiser); also by phosphorous acid, on the application of heat, forming iodine and phosphoric acid (H. Davy). With a small quantity of sulphurous acid, it yields iodine and sulphuric acid; with a larger quantity, hydriodic acid and sulphurous acid; with hydrosulphuric acid, the products are sulphur, water, and iodine, which by a larger quantity of hydrosulphuric acid is converted into hydriodic acid; with hydriodic acid, the products are iodine and water (*Sch.* 70; Gay-Lussac); with hydrochloric acid, provided the quantity of water present is but small, terchloride of iodine, water, and chlorine are produced; with hyponitric acid—only, however, when water is present—iodine and nitric acid (Gaultier de Claubry, *Ann. Chim. Phys.* 46, 221); a case of reciprocal affinity.—Several metals abstract oxygen from iodic acid. (H. Davy.) The oxidation of gold and platinum by iodic acid, which, Sir H. Davy asserted to take place, is denied by Connell and Serullas.—Several organic compounds likewise separate iodine from iodic acid, so that the mixture gives a blue colour to starch: such is the case with hydrosulphocyanic acid and its salts, and therefore also with human saliva (L. Thompson), morphin (Serullas), narcotin, and pyrogallic acid (Duflos, *Schw.* 62, 391).

Combinations. a. With water.

¶ *α. Hydrates of Iodic Acid.* According to Millon (*N. Ann. Chim. Phys.* 19, 400), the crystals obtained by spontaneous evaporation of a concentrated aqueous solution of iodic acid (p. 254) consist, not of the anhydrous acid, but of iodic acid combined with 1 atom of water, IO^5, HO; and these, when heated to 130° (266° F.), or when digested in absolute alcohol, are converted into $3IO^5$, HO, a compound which is insoluble in alcohol, but is reconverted into IO^5, HO by contact with water. Either of these hydrates heated to 170° (338° F.) yields the anhydrous acid, which, by contact with water or alcohol, is converted into the first hydrate, IO^5 HO. (*Comp.* Rammelsberg, *Pogg.* 72, 417.) ¶

β. Aqueous Iodic Acid. The anhydrous acid deliquesces in damp air (H. Davy): according to Serullas, it is permanent in the air, but extremely soluble. The solution, which is transparent and colourless, is not altered by light; it may be evaporated to the consistence of a syrup. At 200°, it is resolved into iodine and oxygen gas (Gay-Lussac): when carefully evaporated, it first becomes syrupy, then pasty, and finally loses all its water without undergoing decomposition. (H. Davy.) Sulphuric acid and nitric acid diminish the solvent power of water upon iodic acid, and cause it to separate in the crystalline form from its concentrated solution. (Serullas.) These crystalline precipitates were regarded

by Davy as intimate compounds of iodic acid with sulphuric or nitric acid. Serullas, on the contrary, has shewn that the sulphuric or nitric acid is attached to them merely by mechanical adhesion; and that it may be almost entirely removed by washing with water and pressing between blotting-paper. Alcohol likewise partly precipitates iodic acid from its aqueoussolution. (Serullas.) Aqueous iodic acid communicates a blue colour to starch or its solution in boiling water, on the addition of sulphurous acid, hydrosulphuric acid, protochloride of tin, or other deoxidizing agents.

¶ *b.* With sulphuric acid.—When iodic acid is digested in oil of vitriol (SO^3HO) nearly at the boiling point, a white, pulverulent mass, having a mother-of-pearl lustre, separates on cooling. No gas is evolved. The composition of this substance is $3SO^3, HO + IO^5, HO$. With more dilute acid ($SO^3, 3HO$), another compound is obtained, consisting of $3(SO^3, 3HO) + IO^5, HO$. (Millon, *N. Ann. Chim. Phys.* 12, 330.) ¶

c. Iodic acid combines with salifiable bases, forming salts called *Iodates.* These compounds are obtained: 1. By bringing iodine in contact with an alkali and water, and removing the metallic iodide or hydriodate formed at the same time, by digestion in alcohol.—2. By direct mixture of iodic acid with a salifiable base.—3. By bringing the aqueous acid in contact with metals, which become oxidated, partly at the expense of the water, partly at the expense of the acid. Some iodates contain one, some two, and others three atoms of acid to one atom of base. When heated, these salts either give up 6 atoms of oxygen, but no iodine, and are converted into metallic iodides (KO, IO^5); or they part with their iodine and 5 atoms of oxygen, and are reduced to metallic oxides (BaO, IO^5), accordingly as the metal has greater affinity for iodine or for oxygen. Some iodates detonate when heated with combustible bodies, *e. g.* on red-hot coals,—sometimes even when merely struck,—the loosely combined oxygen of the iodic acid, and sometimes also that of the metallic oxide passing over to the combustible body, with development of light heat; but the detonation is much weaker than that produced by chlorates or nitrates. The aqueous solution of an iodate mixed with sulphurous acid yields iodine and sulphuric acid, part of which combines with the base. (Gay-Lussac.) With hydrosulphuric acid, the solution of an iodate yields hydriodic acid, water, sulphur, and a sulphate (H. Rose); with hydriodic acid, it yields a metallic iodide, iodine, and water; with a dissolved iodide (or hydriodate), if both compounds contain weak bases, (*e.g.* oxide of zinc,) or if an acid is added which takes hold of the base —the products are water, a metallic oxide, and iodine (Gay-Lussac):

$$ZnO, IO^5 + 5(ZnO, HI) = 5HO + 6ZnO + 6I.$$

With hydrochloric acid the iodates form water, a metallic chloride, terchloride of iodine, and free chlorine; and the metallic chloride thus produced often enters into combination with the terchloride of iodine. (Filhol):

$$KO, IO^5 + 6HCl = 6HO + KCl, + ICl^3 + 2Cl.$$

Arsenious acid, with the aid of heat, and likewise protochloride of tin, separate iodine from aqueous solutions of the iodates. (Simon.) Dilute sulphuric at a boiling heat separates the iodic acid from these salts. (Gay-Lussac.) When an aqueous solution of an iodate is heated with nitric acid, that acid at first takes hold of the base, either wholly or in part; but when the solution is evaporated to dryness and more strongly heated, the less volatile iodic acid drives out the nitric acid. (Penny, *Ann. Pharm.*

37, 203.) Iodates heated with strong hydrochloric acid and mercury, or with oil of vitriol and scale oxide of iron in the state of powder, impart a blue colour to gelatinous starch, in consequence of the separation of iodine which takes place. (Wackenroder, *N. Br. Arch.* 24, 148.) Most iodates are little or not at all soluble in water; the only salts of the class that are easily soluble are the normal iodates of ammonia, potassa, and soda; the solutions of these salts give, with somewhat concentrated solutions of strontia and lime salts, and with dilute solutions of baryta, lead, and silver salts, a white, crystalline-granular precipitate. The silver precipitate is easily soluble in ammonia (Gay-Lussac); very slightly in nitric acid. (Benckiser.)

c. Iodic acid is very slightly soluble in alcohol. (Serullas.)

D. Periodic or Hyperiodic Acid. IO^7.

Überiodsäure, Acide oxiodique.

Formation. When chlorine is passed through a moderately warm mixture of iodate of soda and caustic soda, periodate of soda is formed, and falls down in the form of powder when the liquid is evaporated.

Preparation. 1. A solution of periodate of soda in cold dilute nitric acid is precipitated by nitrate of silver; the yellow precipitate, which is bibasic periodate of silver, is dissolved in hot dilute nitric acid, and the solution concentrated by evaporation at a moderate heat, till normal periodate of silver crystallizes out. After pouring off the mother-liquid, which contains nitrate of silver, the normal periodate of silver is digested in cold water, which extracts half the acid; the solution is then filtered and evaporated. (Magnus & Ammermüller.)—2. The soda-salt is dissolved in the smallest possible quantity of nitric acid, gently warmed and dilute; the solution mixed with nitrate of lead, which precipitates periodate of lead; and the precipitate, after being washed and diffused in water, decomposed by digestion with a quantity of sulphuric acid, not quite sufficient for its complete decomposition. Any excess of sulphuric acid remains mixed with the periodic acid, and prevents its crystallization: excess of periodate of lead does no harm, not imparting any lead to the liquid. The liquid is merely decanted from the sulphate of lead, because filtering-paper might reduce a portion of the acid to the state of iodic acid. The solution evaporated at a gentle heat yields hydrated crystals which lose their water of crystallization at 160° (320° F.). (Benckiser.)

Properties. White mass, fusible by heat.

Calculation.				Vol.
I	126	69·23	Vapour of iodine	2
7O	56	30·77	Oxygen gas	7
IO^7	182	100·00		

($I^2O^7 = 2 . 789·75 + 7 . 100 = 2279·50$. Berzelius.)

Decompositions. 1. According to Benckiser, periodic acid when heated to 188° or 190° (370°—374° F.) evolves oxygen with great rapidity, and is converted into iodic acid, which, when subjected to a stronger heat, is resolved into oxygen and vapour of iodine.—2. With hydrochloric acid, periodic acid yields chlorine, water, and iodic acid. (Magnus & Ammermüller.)

$$IO^7 + 2HCl = IO^5 + 2HO + 2Cl.$$

3. The aqueous solution of the acid may be boiled without undergoing decomposition. At a moderate heat, it oxidizes phosphorus, forming phosphoric oxide and phosphoric acid; with zinc, it forms oxide of zinc and iodine; with iron, ferroso-ferric oxide and iodine; with copper, iodate of copper; and with mercury, dinoxide of mercury and iodine. Acetic acid and formic acid precipitate iodine from the solution on boiling, and at the same time form water and carbonic acid: the same action is more slowly produced by oxalic and tartaric acid. Alcohol and ether do not exert any decomposing action. (Benckiser.)

Combinations. a. With Water. α. *Crystallized Periodic Acid.* Colourless crystals, permanent in the air, and appearing to be oblique rhombic prisms. At 130° (266° F.) they fuse without decomposition; and on cooling, the acid solidifies in a crystalline mass. (Benckiser.) β. The acid is readily soluble in water, and deliquesces quickly in moist air. (Benckiser.)

b. With Salifiable Bases. *Periodates, Hyperiodates, Oxiodates.* Some of these salts are normal or monobasic, others bibasic. The normal salts, when heated to redness, evolve oxygen gas and leave metallic iodides; the bibasic salts are resolved into a mixture of iodide and oxide, or reduced metal. Normal periodate of soda loses 6 atoms of oxygen at a low red heat (p. 253), and the other two at a higher temperature. The periodates certainly detonate with combustible bodies. Most of them are difficultly or not at all soluble in water. The solution of the normal soda-salt precipitates bibasic periodates from solutions of baryta, lime, lead, and silver salts, while the liquid acquires an acid reaction. The silver precipitate is of a light-yellow colour, and when warmed with water, becomes dark red. All periodates dissolve with tolerable facility in dilute nitric acid. (Benckiser.)

c. Periodic acid dissolves with tolerable facility in alcohol and ether.

¶ Other compounds of iodine and oxygen have been obtained by Millon. (*N. Ann. Chim. Phys.* 12, 330; abstr. *Ann. Pharm.* 52, 236.) When iodine is rubbed up in a mortar with nitric acid containing 1 or 2 atoms of water, a bulky yellow powder is obtained which appears to be a compound of nitric acid with an oxide of iodine. In contact with water, it is immediately resolved into nitric acid, iodic acid, and iodine: the same decomposition is brought about by the aid of heat. If the action of the nitric acid be long continued, the compound is wholly converted into iodic acid. By treating it with dilute alcohol, a small quantity of a yellow substance is obtained, which appears to be composed of IO^4: this substance Millon calls *Hypo-iodic acid.*

By heating a mixture of 30 parts iodic acid and 150 sulphuric acid, till a few bubbles of oxygen gas are given off, a considerable quantity of a scaly, sulphur-yellow substance is formed in the boiling liquid: this substance appears to consist of $4IO^5 + IO^4 + SO^3, HO$. If the boiling be continued for longer time, the evolution of oxygen goes on, and crystals are formed having a much deeper yellow colour than the preceding: the composition of these crystals appears to be: $2IO^5 + IO^4 + SO^3, HO$. Water decomposes both these compounds into sulphuric acid, iodic acid and iodine.

By continuing the action of the sulphuric acid till iodine begins to escape together with the oxygen, two other compounds are obtained, to

which Millon has assigned the formulæ: $IO^4 + 2SO^3, HO$ and $I^5O^{19} + 10SO^3, HO$. These substances, when subjected to the action of moist air, appear to yield the compounds IO^4 and I^5O^{19} in the separate state: to the latter Millon gives the name of *Sub-hypoiodic acid.* ¶

Iodine and Hydrogen.

A. Hydriodous Acid. HI^2.

Iodured Hydriodic acid, Acide hydriodique ioduré, Hydriodige Säure.

Formed when aqueous solution of hydriodic acid is brought in contact with excess of iodine: when the same solution is exposed to the air, the oxygen of which deprives the hydriodic acid of part of its hydrogen; also when iodine is brought in contact with paper and other organic substances, the hydrogen of which is with some difficulty taken up by the iodine; and when iodine in excess is brought in contact with any compound of hydrogen which, with a smaller quantity of iodine, yields hydriodic acid.

Hydriodous acid is not known in the separate state.

Calculation.

2I	252	99·60
H	1	0·40
HI^2	253	100·00

This composition is reduced from the experiments of Baup (*J. Pharm.* 9, 40); according to which it appears that aqueous solution of hydriodic acid, or of hydriodate of potassa, or hydriodate of oxide of zinc, when brought in contact with iodine, dissolves a quantity of it exactly equal to that which the solution itself already contains.

Combinations. a. With Water. *Aqueous Hydriodous Acid.* Prepared in the way just mentioned. Forms a dark-brown liquid having the smell of iodine and a slightly acid taste. When exposed for some time to the air, the oxygen of which gradually abstracts the hydrogen, it deposits crystallized iodine. (Plisson, Joss, *J. pr. Chem.* 1, 135; Marchand, *Pogg.* 31, 540.)

b. With Salifiable Bases. *Hydriodites.* (Vid. *Metallic Iodides.*)

B. Hydriodic Acid. HI.

Hydriodsäure, Hydriod, Iodwasserstoff-säure, Acide hydriodique, Acide iodhydrique; in the gaseous state: *Hydriodic Acid gas, Hydriodsaures gas, Hydriod-gas, Iodwasserstoff-gas, Gas acide hydriodique, Gas acide iodhydrique.*

Formation. 1. When hydrogen gas and vapour of iodine are passed together through a red-hot tube. (Gay-Lussac.) According to Blundell (*Pogg.* 2, 216), spongy platinum brings about the combination at ordinary temperatures.—2. Next to oxygen, fluorine, chlorine, and bromine, iodine has of all substances the greatest affinity for hydrogen, and consequently abstracts that element from most of its combinations, viz. from phosphuretted hydrogen, hydrosulphuric acid, ammonia, and many organic compounds, *e. g.* alcohol, ether, and volatile oils—the result being in all

cases the formation of hydriodic acid. (Gaultier; Colin.)—3. Iodine does not decompose water, even at a red heat, or at all events, produces mere traces of iodic and hydriodic acids. (Gay-Lussac.) If, however, there is likewise present any substance that can take up the oxygen of the water, hydriodic acid is produced in abundance. Hence water and iodine, in contact with phosphorus, form hydriodic acid and phosphorous acid (Gay-Lussac): with hypophosphorous acid, they form hydriodic acid and phosphorous acid (Dulong): with sulphurous acid, only however when a considerable quantity of water is present, they yield hydriodic and sulphuric acid; whereas if the liquid be concentrated, sulphurous and hydriodous acids are produced: dry hydriodic and sulphurous acid gases have no action on each other. (Soubeiran, *J. Pharm.* 13, 421.) With sulphites, if largely diluted, the products are hydriodic acid and a sulphate; similarly with hyposulphites; with arsenious acid, hydriodic acid and arsenic acid; with stannous salts, hydriodic acid and a stannic salt; and with certain metals, hydriodic acid and a metallic oxide.

Preparation. 1. *In the gaseous state.* *a.* 1 part of phosphorus and 9 parts of iodine are moistened with a small quantity of water or aqueous hydriodic acid, or covered with moistened glass-powder, and heated in a retort connected with the mercurial trough. Towards the end of the operation, hydriodate of phosphuretted hydrogen may sublime.—*b.* 1 part of phosphorus is gently heated with 14 parts of iodide of potassium, 20 of iodine, and a small quantity of water. If the evolution of gas becomes too violent, the vessel must be plunged into cold water; if it becomes too slow, heat must be again applied. (Millon, *J. Pharm.* 28, 299.)

$$2KI + 5I + P + 7HO = 2KO, PO^5 + 7HI.$$

(*Vid.* Deville's method; *Ann. Chim. Phys.* 75, 46.)

2. *In the liquid state.* Iodine and persulphide of hydrogen, which, when they come in contact, unite and form a yellowish-brown liquid, are placed together in the closed end of a dry glass tube; and at a short distance from them, in a bend of the tube, is placed a small quantity of water. If the tube be then sealed, and the first-mentioned liquid brought in contact with the water, decomposition takes place, resulting in the separation of sulphur and hydriodic acid; and a considerable portion of the latter condenses in the liquid state. (Kemp, *Phil. Mag. J.* 7, 444.)

3. *In the solid state.* Liquid hydriodic acid solidifies at a temperature of $-51°$ C. $= -59{\cdot}8°$ F. (Faraday. *Vid.* I., 287.)

Properties. In the solid state, hydriodic acid is perfectly transparent and colourless, and intersected with fissures, like ice. (Faraday.)

In the liquid state it is yellowish. (Kemp.) In the gaseous state it is colourless. Sp. gr. (I., 279.) Reddens litmus strongly; has a very sour smell like that of hydrochloric acid gas; very suffocating when inhaled; produces dense white fumes in the air; does not support combustion, and is not itself combustible.

Calculation.				Vol.	Sp. gr.	Vol.	Sp. gr.
I	126	99·21	Vapour of Iodine	1	8·7356	= ½	4·3678
H	1	0·79	Hydrogen gas	1	0·0693	= ½	0·0346
HI	127	100·00	Hydriodic acid gas	2	8·8049	= 1	4·4024

(HI = 6·24 + 789·75 = 795·99. Berzelius.)

Decompositions. 1. A mixture of hydriodic acid and oxygen gases

passed through a red-hot porcelain tube is resolved into water and iodine. (Gay-Lussac.)—2. The following compounds give up their oxygen to the hydrogen of the hydriodic acid, forming water and separating iodine. Hydrated peroxide of hydrogen is converted by it into water. (Thénard.)—Sulphurous acid gas and hydriodic acid gas yield water, sulphur, and iodine:

$$SO^2 + 2HI = 2HO + S + 2I.$$

If water is present, the two acids have no action on one another. (Dumas.) When mixed in the state of aqueous solution, they form a yellow liquid, the colour of which is brighter in proportion as the acids are more concentrated. When exposed to the air, it gradually becomes coloured from top to bottom, in consequence of separation of iodine: a fresh addition of sulphurous acid colours it yellow again; but the colour becomes continually weaker, and at length sulphur is separated. (Saladin, *J. Chim. Med.* 7, 528.)—Oil of vitriol and hydriodic acid gas or concentrated solution of hydriodic acid, yield iodine, water, and sulphurous acid. (Gay-Lussac.)

$$SO^3 + HI = SO^2 + HO + I.$$

On the addition of water, sulphuric acid and hydriodic acid are again produced (reciprocal affinity, I., 128). *Soubeiran.*—Aqueous iodic acid and hydriodic acid yield water and iodine (*Sch.* 78).—Hypochlorous acid decomposes hydriodic acid, both in the gaseous form, and in the state of aqueous solution. (Balard.)—Nitric acid yields iodine, water, and nitric oxide. (Gay-Lussac.)—Salts of ferric oxide are converted by hydriodic acid into salts of ferrous oxide, iodine being at the same time precipitated. (Gay-Lussac.)—3. Chlorine gas, in small quantity, converts hydriodic acid gas into hydrochloric acid and iodine;

$$Cl + HI = HCl + I;$$

in larger quantity, into hydrochloric acid and chloride of iodine; *e. g.*

$$4Cl + HI = HCl + ICl^3.$$

(Gay-Lussac.) In a similar manner, bromine and hydriodic acid gas yield hydrobromic acid gas and iodine, the action being attended with evolution of heat. (Balard.)—4. Potassium, zinc, iron, mercury, and other metals, immersed in this gas, are converted into iodides, 1 volume of hydrogen being at the same time liberated from 2 volumes of hydriodic acid gas. (Gay-Lussac.)—5. With most basic metallic oxides, hydriodic acid forms water and a metallic iodide. Some of these iodides separate immediately; so that, with the salts of certain metallic oxides, aqueous hydriodic acid forms precipitates consisting of metallic iodides and distinguished by the following colours: Oxide of bismuth, brown; oxide of lead, orange-yellow; mercurous oxide, greenish-yellow; mercuric oxide, scarlet; oxide of silver, yellowish-white. Other metallic iodides remain dissolved in the liquid, and in that state may be regarded as hydriodates of metallic oxides. With metallic peroxides, *e. g.* the peroxide of manganese or of lead, hydriodic acid forms a metallic iodide (or hydriodate), water, and free iodine; *e. g.*

$$PbO^2 + 2HI = PbI + 2HO + I.$$

Combinations. *a.* With Water. *Aqueous Hydriodic acid, Hydriodic acid Water, Ioduretted Hydrogen Water.* Water absorbs hydriodic acid gas very rapidly and in large quantity. *Preparation.* 1. Iodine is distilled with phosphorus and a large quantity of water.—2. Hydrosulphuric acid gas is passed into water in which iodine is diffused—the liquid being

well agitated all the while—till the iodine has disappeared and the liquid, which was brown at first, has become colourless: the liquid is then filtered and heated to commencing ebullition in order to expel the excess of hydrosulphuric acid. (Gay-Lussac.) Since the sulphur, as it precipitates, envelopes the iodine which still remains undissolved, Le Royer & Dumas recommend the process of saturating water with iodine—decanting the liquid from the undissolved portion—converting the dissolved iodine into hydriodic acid by means of sulphuretted hydrogen—digesting in this liquid a fresh portion of iodine, which dissolves much more abundantly in the hydriodic acid already produced—decanting again—once more saturating with sulphuretted hydrogen—again digesting with iodine, &c. &c. Another method is that of Stratingh, which consists in passing hydrosulphuric acid gas through a solution of iodine in 16 parts of alcohol, filtering, diluting with 32 parts of water, and freeing the product by distillation from alcohol and excess of hydrosulphuric acid. The acid prepared in this manner is liable, however, to be mixed with a product of disagreeable odour, arising from the action of the hydrosulphuric acid on the alcohol.—3. Iodide of barium dissolved in water is exactly decomposed by the equivalent quantity of sulphuric acid, and the product separated by filtration from sulphate of baryta. (Glover, *Phil. Mag. J.* 19, 92.)—4. Granulated lead is agitated with iodine and water till the liquid becomes colourless; hydrosulphuric acid gas is then passed through, and the liquid decanted. (Joss, *J. pr. Chem.* 1, 133.) The aqueous solution of the acid obtained by either of these methods may be concentrated by heating it in a retort.

Hydriodic acid water is colourless; has a specific gravity of 1·700 when concentrated. The concentrated solution boils between 125° and 128° (257° and 262·4° F.), and may be distilled over without previously evolving gas. Its odour resembles that of the gas; and its taste is first pungent, afterwards astringent and sour. When concentrated, it fumes on exposure to the air. [For its decomposition by electricity, *vid.* I., 455.] When exposed to the air, it gives off hydrogen, and is at first quickly converted into a brown solution of hydriodous acid, which is afterwards slowly and completely decomposed, depositing beautiful crystals of iodine. The other modes of decomposition are given on page 263, 2, 3, 5. A small quantity of chlorine water turns it brownish red and precipitates iodine; a larger quantity decolorizes it again. The concentrated solution is turned yellow by oil of vitriol, and on the application of heat, becomes brown-red, iodine being precipitated and iodine vapour evolved. Hydriodic acid water imparts a blue colour to starch on the addition of oil of vitriol, or of a small quantity of chlorine, or nitric acid, or chlorate of potassa with hydrochloric acid.

b. With Phosphuretted Hydrogen.

c. With Salifiable Bases, forming the *Hydriodates*: vid. *Metallic Iodides.*

Charcoal has no action on iodine, even at a white heat. (H. Davy.) The compounds of iodine with carbon and hydrogen together, will be described under *Organic Chemistry.*

Iodine and Boron.

Vapour of iodine, passed over an ignited mixture of charcoal and boracic acid, yields a small quantity of a yellow sublimate, probably *Iodide of Boron.* (Inglis.)

Iodine and Phosphorus.

A. Iodide of Phosphorus. Combination takes place at ordinary temperatures, and according to Gazzaniga (*Bibb. Univ.* 54, 186), even at —24°, with great evolution of heat, which, if the air has access to the materials, sets fire to the phosphorus. (Compare Traill, *Ed. Phil. J.* 12, 217; also *Ann. Phil.* 24, 153.)

a. 1 *part of phosphorus with* 24 *of iodine.* Black mass, fusing at 46°, and forming a brown solution in water. (Does this solution contain phosphorous and hydriodous acids?.)—b. 1 *part of phosphorus with* 16 *of iodine.* Dark grey, crystallized; fuses at 29°; dissolves in water forming phosphorous and hydriodic acid (perhaps also a small portion of hydriodous acid is formed).—c. 1 *part of phosphorus with* 8 *of iodine.* Orange-yellow mass, fusing at 100°, volatile at a higher temperature; dissolves in water, forming phosphorous and hydriodic acid, with evolution of phosphuretted hydrogen and precipitation of flakes of phosphorus. (Gay-Lussac.)

B. Compound of Iodic acid and Phosphoric acid. The two acids mixed together in the state of aqueous solution form a yellow crystalline mass. which may be sublimed. (H. Davy.) Serullas doubts the existence of this compound.

C. Hydriodate of Phosphuretted Hydrogen. 1. When hydriodic acid gas and phosphuretted hydrogen, both dried as completely as possible, are brought together in a vessel, they unite and form colourless crystals. (Houton Labillardière, *Ann. Chim. Phys.* 6, 304; also *Gilb.* 68, 253; also *N. Tr.* 3, 1, 189.)—2. Phosphorus and iodine in nearly equivalent proportions are heated in a retort with a small quantity of water; hydriodic acid gas is first evolved, and afterwards hydriodate of phosphuretted hydrogen sublimes. Probably, hypophosphorous acid is produced in the first instance, and is converted, together with the excess of water, into phosphoric acid and phosphuretted hydrogen:

$$2P + 2I + 5HO = PO^5 + PH^3, HI + HI.$$

The product actually obtained is however much less than this calculation would lead us to expect, because the greater portion of the hydriodic acid escapes before the decomposition of the hypophosphorous acid is complete. Guy-Lussac first obtained in this manner a white sublimate crystallized in cubes, and evolving phosphuretted hydrogen when put into water; he did not however examine it further. Serullas (*J. pr. Chem.* 8, 6; also *Schw.* 64, 238; also *Pogg.* 24, 345) puts into a retort 4 parts of iodine and 1 part of phosphorus mixed with a small quantity of coarsly pounded glass (introducing the mixture through the tubulure)—moistens the mixture with rather more than ½ pt. water,—and quickly connects the retort by means of a stopper with a glass tube cooled by wet linen. The evolution of hydriodic acid and hydriodate of phosphuretted hydrogen begins immediately, and is kept up by gently heating the retort. The sublimed compound is driven by means of a red-hot coal from the neck of the retort into the tube, where it collects in the form of a hard crystalline crust. This crust is detached from the retort by means of a sharp metal rod, and purified by a second distillation in the same apparatus. The quantity of the compound obtained is at most equal to that of the phosphorus used.—H. Rose (*Pogg.* 24, 151) heats in a retort 1 part of phosphorus with 4 parts of iodine and a very small quantity of water (or

better, of aqueous hydriodic acid)—passes the vapours into a long glass tube—and, after the whole of the hydriodate of phosphuretted hydrogen has been driven into the tube by the application of heat, detaches the tube from the retort—passes a stream of air previously dried by chloride of calcium through it, in order to expel the hydriodic acid gas—and seals it at both ends.

Large, transparent, colourless crystals having the lustre of diamond. According to Gay-Lussac and Houton Labillardière, they form cubes; according to H. Rose (*Pogg.* 46, 636), square prisms with the terminal edges and angles truncated (*Fig.* 34). By gentle heating in close vessels, the crystals may be sublimed backwards and forwards without fusing. (H. Rose.) Boiling point, about 80°. (Bineau.)

		Calculation.		H. Rose.
PH^3	....	34·4	21·31	20·91
HI	....	127·0	78·69	79·09
PH^3, HI	....	161·4	100·00	100·00

According to Bineau.	Vol.		Sp. gr.
Phosphuretted Hydrogen gas	½	....	0·5962
Hydriodic acid gas	½	....	2·2012
Vapour of Hydriodate of Phosphuretted Hydrogen	1	....	2·7974

Houton Labillardière distinguishes two compounds, according as the more inflammable or the less inflammable phosphuretted hydrogen is used in the preparation by method 1: the compound exhibits the same properties in both cases; but in the former, it appears to contain 1 vol. hydriodic acid gas with ½ vol. of the more inflammable, and in the latter, 1 vol. hydriodic acid with 1 vol. of the less inflammable gas. But H. Rose and Leverrier (*Ann. Chim. Phys.* 60, 192) have shown that the more inflammable gas likewise combines with hydriodic acid gas in equal volumes, and that the two compounds are perfectly identical.

Decompositions. The vapour of this compound may be passed, without undergoing decomposition, through a red-hot tube containing borax in a state of fusion. (Serullas.) According to H. Rose, the compound deposits phosphorus even when gently heated, and the crystals thereby acquire a yellowish tinge. 1. Water and watery liquids, such as solution of ammonia or potassa, take up the hydriodic acid and liberate the phosphuretted hydrogen, rapidly, with effervescence, and in the less inflammable state. (Houton; H. Rose.) Even concentrated solution of ammonia almost always liberates the gas in the less inflammable condition. (H. Rose.) When exposed to the air, especially to moist air, the crystals deliquesce, with evolution of phosphuretted hydrogen.—2. Ammoniacal gas forms hydriodate of ammonia, and liberates a quantity of phosphuretted hydrogen equal in volume to the ammoniacal gas absorbed. (Houton.)—3. Oil of vitriol decomposes the compound rapidly, with simultaneous evolution of hydrosulphuric acid and sulphurous acid gases, which mutually decompose each other, and separation of sulphur, phosphorus, and iodine,—while the oil of vitriol retains in solution an acid of phosphorus, and likewise a portion of hydriodic acid still in a state of decomposition. 4. Iodic, bromic, chloric, and nitric acids, and the anhydrous salts of the first three, set fire to hydriodate of phosphuretted hydrogen at ordinary temperatures. Nitrate of silver exerts a violent action, producing great rise of temperature and forming iodide and phosphate of silver. Perchloric acid, perchlorate of potassa, and nitre decompose the compound

only when heat is applied, and even then but slowly. (Serullas.)—5. Oxide of silver in contact with this compound produces great development of heat and is converted into iodide of silver, with evolution of spontaneously inflammable phosphuretted hydrogen gas. Protobromide of mercury produces iodide of mercury and hydrobromate of phosphuretted hydrogen, with which however a quantity of hydriodate of phosphuretted hydrogen still remains mixed. Protochloride of mercury yields iodide of mercury, hydrochloric acid gas, and phosphuretted hydrogen. Cyanide of mercury or cyanide of potassium yields a metallic iodide, hydrocyanic acid, and phosphuretted hydrogen gas. (Serullas.)—6. With hot absolute alcohol, the compound yields hydriodic ether and phosphuretted hydrogen gas. It is also decomposed by contact with sulphovinate of oil of wine. (Serullas.) Hydriodate of phosphuretted hydrogen is not decomposed by oxygen, carbonic acid, hydrosulphuric acid, or hydrochloric acid gas, or by mercury (Houton); neither is it decomposed by hot glacial acetic acid. (Serullas.)

Iodine and Sulphur.

A. Iodide of Sulphur.—1. Sulphur combines with iodine on the application of heat, even under water, and with slight rise of temperature. (Gay-Lussac.)—2. Aqueous hydriodic acid mixed with chloride of sulphur yields hydrochloric acid and a precipitate of iodine. (Inglis.) From aqueous solution of terchloride of iodine, hydrosulphuric acid throws down a cinnabar-coloured precipitate of iodide of sulphur. (Grosourdy, *J. Chim. Méd.* 9, 429.)

The compounds obtained by method (1) are blackish-grey, brilliant, and exhibit a radiated fracture like that of crude sulphide of antimony; they fuse below 60°. (Gay-Lussac.) When heated out of contact of air, they evolve pure vapour of iodine, according to Gay-Lussac; but according to H. Rose (*Pogg.* 27, 115), they give off an iodide of sulphur containing 11·24 per cent. of sulphur. They are not soluble in water. (Gay-Lussac.) Alcohol, in a few minutes, extracts the whole of the iodine from them. (Inglis.)

One part of sulphur to 9 parts of iodine: smells faintly of iodine.—1 part (1 At.) sulphur to 7·9 parts (1 At.) iodine: Blackish-grey; of lamellated and radiated texture; smells faintly of iodine.—1 part (2 At.) sulphur to 4 parts (1 At.) iodine: Decidedly crystalline.—1 part sulphur to 1 or ½ part iodine: somewhat dense masses, which turn white on exposure to the air. (N. E. Henry, *J. Pharm.* 13, 403.)

B. Sulphate of Iodine.—Anhydrous sulphuric acid forms a greenish-blue liquid with iodine. (Bussy.) According to Fischer (*Pogg.* 16, 121), the compound is sometimes brown, sometimes green, sometimes blue; the green and blue colours are transient; the brown, persistent.—With the minimum quantity of sulphuric acid, the compound is brown; with a larger quantity, blue; and with a still larger quantity, green. (Wach.) If a bent glass tube containing 1 part of iodine in one arm, and 10 parts of anhydrous sulphuric acid in the other be sealed, and heat applied to the arm containing the sulphuric acid, the portions of sulphuric acid vapour which first pass over, form with the iodine a viscid brown liquid, which, by taking up the rest of the acid, is subsequently converted into a crystalline mass of a beautiful green colour. This substance melts at 37° to an oily liquid, and solidifies at 12·5° in bundles of fibres. It

boils in the sealed tube at 107·5°, sulphuric acid distilling over, and—if the other arm of the tube is immersed in a freezing mixture—condensing in it as a white crystalline mass: and the liquid, as it parts with the acid, becomes first blue and afterwards brown. Finally, iodine sublimes and crystallizes on the solidified sulphuric acid, and by the application of heat may be made to recombine with it, and form the green compound. One part of iodine and 15 of sulphuric acid likewise form a beautiful green compound, which behaves in a similar manner when distilled. If one arm of the tube contains 1 part of iodine and 1 part of sulphur, the other, 20 parts of anhydrous sulphuric acid, and the whole is left to stand over night at the ordinary temperature of the air, the sulphur acquires a carmine colour. If the sulphuric acid arm be warmed, while the other arm is kept in a freezing mixture, the sulphur and iodine form a thin red-brown liquid, which moves about as if it were boiling, and gradually becomes, first brown, then brownish-green, and crystallizes. When taken out of the freezing mixture, it changes in the course of four weeks to a beautiful green liquid (probably consisting of sulphate of iodine with sulphurous acid), which crystallizes in the cold. Sulphurous acid may be distilled from it, but when separated in this manner, may be made to recombine with the residue. (Wach, *Schw.* 50, 37.) From a solution in hot dilute sulphuric acid, iodine crystallizes in needles on cooling.

C. Sulphate of Hydriodic Acid. Anhydrous sulphuric acid rapidly absorbs hydriodic acid gas, and deliquesces with it to a brown-red liquid. (Aimé, *J. Pharm.* 21, 88; also *J. pr. Chem.* 6, 79.)

D. Iodurettted Persulphide of Hydrogen. Dry iodine dissolves in persulphide of hydrogen, forming a liquid of a yellowish-brown colour. The smallest quantity of water resolves the compound into sulphur and hydriodic acid (p. 236). Kemp.

E. Iodurettted Bisulphide of Carbon. Iodine dissolves abundantly in bisulphide of carbon, imparting a deep amethyst colour to the liquid; even 0·001 iodine produces a sensible amethyst tint, and $\frac{1}{18,100}$ a pale rose-colour. (Lampadius, *Gilb.* 58, 443, and *Schw.* 31, 253.) A very large quantity of iodine makes the compound black-brown, and of a thick oily consistence; water shaken up with it acquires a pale violet tint, but remains clear, and does not take up hydriodic acid. (Zeise, *Schw.* 36, 63.) A solution saturated while hot deposits iodine on cooling; it does not conduct electricity. (Solly, *Phil. Mag. J.* 8, 132.)

Iodine and Selenium.

Iodide of Selenium. The two substances heated together in equivalent proportions readily fuse into a black-grey mass, from which absolute alcohol abstracts the whole of the iodine. (Trommsdorff, *N. Tr.* 12, 2, 45.)

Other Compounds of Iodine.

A. With Bromine.—B. With Chlorine.—C. With Nitrogen.—D. With Ammonia.

E. With metals, forming the *Metallic Iodides.* These compounds are

formed.—1. When iodine comes in contact with a metal—frequently even at ordinary temperatures, as in the case of mercury. The combination is attended with development of heat, sometimes with flame, which is coloured violet by the iodine vapour (*e. g.* potassium, sodium).—2. When hydriodic acid comes in contact with metals whose affinity for iodine exceeds that of hydrogen.—3. When vapour of iodine is passed through a red-hot tube containing a metallic oxide, the metal of which (potassium, sodium, lead or bismuth) has a stronger affinity for iodine than for oxygen—in which case, the oxygen is expelled in the form of gas.—4. When hydriodic acid is brought in contact with metallic oxides; in which case, sometimes at ordinary temperatures (oxide of lead), sometimes by crystallization (potassa), sometimes on the application of heat (oxide of zinc), an anhydrous metallic iodide and water are produced.

All iodides are destitute of metallic lustre; some of them are very beautifully coloured. Their specific gravity is often lower than the mean specific gravity of their constituents: such is the case with the iodides of potassium, lead, copper, and silver. (Boullay.)

But few metallic iodides are decomposed by heat alone; the iodides of gold, silver, platinum, and palladium, however, give up their iodine when heated. Most metallic iodides when ignited in open vessels, so that the air has access to them, give up their iodine, and are converted into oxides; such, however, is not the case with the iodides of potassium, sodium, bismuth, and lead. Chlorine, at a red heat, decomposes the metallic iodides, converting them into chlorides, and either setting the iodine free or forming chloride of iodine. (H. Davy.) Bromine acts in a similar manner. Chlorine-water likewise liberates the iodine. Hydrochloric acid gas decomposes metallic iodides at a red heat, forming hydriodic acid gas and a metallic chloride. Concentrated sulphuric and nitric acid, and likewise bisulphate of potassa, decompose all metallic iodides on the application of heat, the products being iodine, which escapes in violet vapours (which give a blue colour to paper moistened with starch), and a sulphate or nitrate of the corresponding metallic oxide. When this change is produced by nitric acid, hyponitric acid is formed at the same time; sulphuric acid and bisulphate of potassa evolve sulphurous acid, sometimes, also, sulphuretted hydrogen. Oil of vitriol or bisulphate of potassa with peroxide of manganese, peroxide of lead, or chromate of potassa produces the same decomposition, but without evolution of sulphurous acid (p. 264.). A bead of microcosmic salt saturated with oxide of copper communicates a beautiful green colour to the blow-pipe flame on the addition of a metallic iodide. (Berzelius.) Metallic iodides agitated with oil of vitriol and bisulphide of carbon, communicate an amethyst-red tint to the latter.

Very few metallic iodides remain unaltered in contact with water: such, however, is the case with the iodides of bismuth, lead, copper, and several of the noble metals. Some of them are converted by water into an oxide which is precipitated, and hydriodic acid which dissolves in the water (iodide of tin): or into a precipitated compound of iodide and oxide of the metal, and a solution of the iodide in aqueous hydriodic acid (the iodides of antimony and tellurium). Most metallic iodides are perfectly soluble in water; and the solution may be regarded as containing either the unaltered iodide, or a hydriodate of the oxide formed by double decomposition (*e. g.* the iodides of the alkali-metals, iron, nickel, cobalt, &c.).

Aqueous Metallic Iodides or *Salts of Hydriodic Acid, Hydriodates, Iodhydrates,* including Hydriodate of Ammonia. These compounds are pro-

duced on dissolving a metallic iodide in water, on bringing iodine in contact with a metal and water, or on digesting a metal or metallic oxide in aqueous hydriodic acid: in the latter case, hydrogen gas is evolved. These compounds are extremely poisonous. When evaporated out of contact of air, they generally leave anhydrous metallic iodides, which partly separate in the crystalline form before the water is wholly driven off. The earthy hydriodates, however, are resolved, on evaporation, into the earthy oxides and hydriodic acid, which escapes. A very small quantity of chlorine colours the solution yellow or brown, by partial decomposition and formation of a salt of hydriodous acid; a somewhat larger quantity takes up the whole of the metal, forming a chloride (or hydrochlorate), and separates the iodine, which then gives a blue colour with starch; a still larger quantity of chlorine gives the liquid a paler colour, and converts the separated iodine into terchloride of iodine, which does not give a blue colour with starch, and frequently enters into combination with the chloride produced. Oil of vitriol and somewhat concentrated nitric acid colour the solution yellow or brown, from formation of hydriodous acid; and if the quantity of the iodide is large, and the solution much concentrated or heated, they separate iodine, which partly escapes in violet vapours. Starch mixed with the solution, even if it be very dilute, is turned blue—permanently, when the decomposition is effected by sulphuric acid; for a time only, when it is effected by nitric acid, especially if that acid be added in large quantity. If the oil of vitriol contains sulphurous acid, which is very likely to be the case with fuming oil of vitriol, it does not produce the blue colour, even when added in large excess. If a liquid in which iodine is present (urine, for example) contains much organic matter, which may decompose the oil of vitriol and form sulphurous acid, it will not produce the blue colour with starch and oil of vitriol unless it be diluted with water. (Dupasquier, *J. Pharm.* 28, 218.) If the solution likewise contains a salt of iodic acid, most acids when mixed with it produce a brown colour and separate iodine; because, by virtue of their affinity for the base of the iodate, they facilitate the mutual decomposition of the hydriodic and iodic acid. The separation of iodine and the blueing of the starch likewise takes place on adding hydrochloric acid to the solution, together with a stannic, ferric, or cupric salt, or a salt of chromic acid. Also, if the solution of the iodide be covered with gelatinous starch, the negative pole of a small voltaic battery immersed in the former, and the positive pole in the latter, the starch is turned blue in the neighbourhood of the positive wire, even if the solution contains a much larger quantity of bromide or chloride than of iodide. (Steinberg, *J. pr. Chem.* 25, 288.) If the aqueous solution of a metallic iodide contains only $\frac{1}{10,000}$ part of iodine, it gives a strong blue colour with dilute gelatinous starch, on the addition of aqua-regia: with $\frac{1}{100,000}$ part of iodine, the precipitate is violet; with $\frac{1}{200,000}$, rose-coloured; and with $\frac{1}{500,000}$, a pale rose-colour is produced after the lapse of a few hours. (Harting, *J. pr. Chem.* 22, 46.) If the solution likewise contains a large quantity of metallic chloride, the blueing of the starch is not readily produced by the addition of nitric acid, in consequence of the formation of chloride of iodine: in this case, a solution of starch in boiling dilute sulphuric acid may be added to the solution of the hydriodate, and then a very small quantity of chlorine water, the liquid being stirred at the same time. (Berzelius.)

The aqueous solution of a hydriodate gives a brown precipitate with salts of bismuth; orange-yellow with lead-salts; dirty white with cuprous salts, and also with cupric salts, especially on the addition of sulphurous

acid; greenish-yellow with mercurous salts; scarlet with mercuric salts; yellowish white with silver salts; lemon-yellow with gold salts; brown with platinic salts, first, however, turning the liquid dark brown-red; and black with palladious salts, even when extremely dilute. All these precipitates consist of metallic iodides; many of them are soluble in excess of the hydriodate; the silver precipitate is insoluble in nitric acid and ammonia.

When iodine is digested in an aqueous solution of a salt of hydriodic acid, the liquid takes up a quantity of iodine equal to that which it already contains. It thereby acquires a dark red-brown colour, and may then be regarded as a solution either of a *Metallic Poly-iodide*, or of a *Hydriodite* or *Salt of Hydriodous acid.* But the affinity by which excess of iodine is retained is very feeble.

Many metallic iodides absorb ammonia in definite proportions.

Some of these compounds unite with the oxides of the corresponding metals, forming *Oxiodides* or *Oxiodurets* (antimony, tellurium).

Metallic iodides combine with one another: these compounds may, according to Bonsdorff's view, be regarded as *Iodine-salts* (p. 9).

E. Iodine likewise combines with several organic substances, as starch, alcohol, ether, oils, cyanogen, &c.

Chapter IX.

BROMINE.

Bromine in general:

Balard. *Ann. Chim. Phys.* 32, 337; also *Schw.* 48, 61; *Pogg.* 8, 114, 319 and 461; *N. Tr.* 14, 1, 80; *Kastn. Arch.* 9, 231.—Further: *Bibl. Univ.* 58, 372; also *J. pr. Chem.* 4, 165.
Liebig. *Schw.* 48, 106; 49, 102.
A. Vogel. *Kastn. Arch.* 10, 119.
Löwig. *Das Brom und seine chemischen Verhältnisse.* Heidelberg, 1829. Further: *Mag. Pharm.* 23, 11; 33, 6.—Also: *Pogg.* 14, 485.—Also: *Repert.* 29, 261.
De la Rive. *Ann. Chim. Phys.* 35, 160; also *Pogg.* 10, 307; also *Kastn. Arch.* 11, 387.
Berzelius. *Pogg.* 14, 164.

Sources of Bromine:

Aschoff. *N. Tr.* 15, 1, 186.—Berthier. *Ann. Chim. Phys.* 77, 417; 79, 164.—Bley. *Br. Arch.* 25, 67.—Boussingault. *Ann. Chim. Phys.* 54, 163.—Brandes. *Br. Arch.* 20, 145.—Daubeny. *Phil. Mag. J.* 6, 323.—Desfosses. *J. Pharm.* 13, 252 and 533.—Emmet. *Sill. Amer. J.* 18, 260.—Ficinus. *Kastn. Arch.* 10, 61; *J. pr. Chem.* 10, 192.—Fromherz. *Schw.* 48, 253.—Fuchs & Fikentscher. *J. pr. Chem.* 5, 321.—Geiger. *Mag. Pharm.* 16, 207; 17, 57.—C. G. Gmelin. *Kastn. Arch.* 10, 59.—Hayes. *Sill. Amer. J.* 20, 161.—Hermbstädt. *Pogg.* 8, 476; 10, 627.—Hermann. *Schw.* 49, 101.—

Von Holger. *Zeitschr. Phys. Math.* 9, 75.—Jonas. *Br. Arch.* 21, 45; *Ann. Pharm.* 26, 346.—Kastner. *Kastn. Arch.* 9, 383; 12, 256.—Kersten. *Schw.* 49, 490.—Liebig. *Kastn. Arch.* 9, 256; *Ann. Pharm.* 41, 145.—Ludwig. *Zeitschr. Phys. Math.* 2, 417.—Meissner. *Schw.* 48, 108. *Berl. Jahrb.* 29, 1, 102.—Menzel & Cochler. *Kastn. Arch.* 12, 252; 13, 336.—Merk. *Repert.* 31, 454.—Mettenheimer. *Schw.* 49, 103.—Morin. *J. Pharm.* 27, 84.—Pleischl. *Zeitschr. Phys. v. W.* 4, 93.—Ragazzini. *J. Chim. Med.* 11, 360.—Sarphati. *Repert.* 59, 314.—Scharf. *J. pr. Chem.* 10, 1.—Spécz. *Pogg.* 10, 510.—Stromeyer. *Kastn. Arch.* 10, 117. *Schw.* 49, 249.—Torosiewicz. *Repert.* 34, 8; 36, 169.—Tünnermann. *Schw.* 49, 249.—A. Vogel. *Kastn. Arch.* 9, 378.—Walchner. *Mag. Pharm.* 17, 56.—Wöhler & Kindt. *Pogg.* 10, 509.

Bromic Acid: Serullas. *Ann. Chim. Phys.* 45, 203.—Rammelsberg. *Pogg.* 52, 79; 55, 63; abstr. *J. pr. Chem.* 22, 364; 25, 225.

Bromide of Phosphorus: H. Rose. *Pogg.* 28, 550.

Hydrobromate of Phosphuretted Hydrogen: Serullas. *Ann. Chim. Phys.* 48, 91; also *J. Chim. Med.* 8, 1; also *Schw.* 64, 238; also *Pogg.* 24, 344.

Bromide of Sulphur: H. Rose. *Pogg.* 27, 111.

Bromide of Selenium: Serullas. *Ann. Chim. Phys.* 35, 349; also *N. Tr.* 16, 2, 197; abstr. *Pogg.* 10, 622.

Metallic Bromides: Serullas. *Ann. Chim. Phys.* 38, 318; also *N. Tr.* 18, 2, 170; abstr. *Pogg.* 14, 111.—O. Henry. *J. Pharm.* 15, 49; also *N. Tr.* 20, 1, 165; also *Kastn. Arch.* 16, 138.—Berthemot. *Ann. Chim. Phys.* 44, 382; also *J. Pharm.* 16, 648; also *Br. Arch.* 37, 322.

Brom, Brome, Bromum.—From βρῶμος, an offensive odour.

History. Discovered by Balard in 1826, in the mother-liquor of sea water, and examined by himself and by Löwig and Serullas in its most important chemical relations or properties.

Sources. As bromide of silver in Mexico, Chili, and at Huelgoeth in Brittany. (Berthier.) In Silesian zinc ore, in very small quantity. (Menzel & Cochler.) In English rock salt, in very small quantity. (*J. Chim. Med.* 17, 131.)

In the following salt springs, probably in combination with sodium, calcium, or magnesium: A salt spring in the Eastern Pyrenees (Balard).—At Bex in Switzerland (Morin).—Salins in the department of the Jura (3840 parts of the mother-liquor contain one part of bromine) (Desfosses).—Rehme near Minden (Aschoff).—Werl in the Duchy of Westphalia (Kersten).—Lüneburg, Pyrmont; in the salt found at Helden, Sülbeck, and Salzgitter (Stromeyer).—Salzuffeln (Brandes).—Schönebeck (Hermann).—Halle on the Salle and Kösen (Meissner).—Dürrenberg (Meissner, Scharf).—Kissingen (Fuchs & Fikentscher).—Nauheim (Tünnermann).—Kreuznach (Liebig); 1000 parts of the mother-liquor contain 0·837 parts of bromine (Mettenheimer).—Rappenau (Geiger, Fromherz).—Wimpfen (Fromherz, Kastner).—Offenau and Jaxtfeld (Fromherz).—Dürrheim (Fromherz, Walchner).—Rosenheim (A. Vogel).—Halle in the Tyrol (Ludwig).—Capo d'Istria (Meissner).—Drohobycz and Starozol in Gallicia (Torosiewicz).—Kenahwa in North America (Em-

met).—Hingham in North America (Hayes).—Several salt springs in the province of Antioquia in New Granada (Boussingault).—Many specimens of sal-ammoniac contain bromine (Merk; Geiger); probably because it has been prepared from the mother-liquor of mineral waters containing that element.

The following mineral waters likewise contain bromine: Thermal springs of Albano (Ragazzini).—Spring of Bourbonne (Desfosses).—Beringer baths in the Harz (Bley).—Ragozy spring at Kissingen (Ficinus).—Wiesbaden (uncertain). *Kastner*.—Homburg (Liebig).—Karlsbad (Pleischl).—Magnesia spring of Püllna (Ficinus).—Goître-water (*Kropfwasser*) of Hall in Austria (Holger).

Sea-water containing bromine: The water of the Mediterranean (Balard).—Sea-water from the Gulf of Trieste (Specz).—From the North Sea (Stromeyer).—From the Baltic (Wöhler & Kindt, Kastner).—One gallon of sea-water, near Marseilles, contains 1·26 grains, and the same quantity near Naples or from the Channel contains 0·915 grains of bromine (Daubeny).—The water of the Dead Sea also contains bromine. (C. G. Gmelin; Hermstädt).—All marine plants of the Mediterranean, and likewise varec, contain bromine (Balard).—Bromine is also found in marine plants on the coast of Holland (Sarphati).—It is likewise present in marine animals; namely, in *Janthina violacea* (Balard); in many varieties of *Rhizostoma* and *Cyana*, in Asterias *rubens*, *Crognon vulgare*, *Mytilus edulis*, and *Pleuronectes Flesus*, in which bromine is far more abundant than iodine (Sarphati); in sponge (Hermbstädt, Jonas); and in sponge-stone (Hermbstädt).—Salted Scotch herrings likewise contain bromine. (Jonas.)

Preparation. 1. The mother-liquor of sea-water (or some other water containing bromine) is freed, by evaporation, from crystallizable salts, and chlorine gas passed through it, as long as the yellow colour increases in depth. The chlorine decomposes the metallic bromide into chloride and free bromine, (or the hydrobromate into hydrochlorate and free bromine), the latter produces the colour: an excess of chlorine would convert the bromine into chloride of bromine, and thereby decolorize the liquid; it must therefore be avoided. The mixture is afterwards shaken with ether, which acquires a hyacinth-red colour by absorbing the bromine, the ethereal solution separated by decantation (or by means of a funnel), and the bromine removed by a concentrated aqueous solution of potash (the ether may be used again to treat the same or a fresh solution). The solution containing bromide of potassium and bromate of potassa is then evaporated to dryness, the residue ignited to decompose the bromide of carbon which is formed at the same time* (*Löwig*); the ignited mass mixed with (⅓ its weight, *Löwig*) peroxide of manganese, and distilled with (one part, *Löwig*) oil of vitriol diluted with half its weight of water; and the distillate collected in a receiver containing sufficient water to cover the end of the retort. Lastly, the bromine is separated from the supernatant watery liquid and rendered anhydrous by distillation with chloride of calcium. When the liquid used in the preparation of the bromine likewise

* The bromine of commerce frequently contains bromide of carbon, probably formed by the action of the bromine on the ether used in its preparation. The quantity of this impurity varies in different samples: one sample from the Schönebeck factory contained between 6 and 8 per cent. The last portions of bromine thus contaminated require a higher temperature for distillation than pure bromine, the boiling point rising from 50° to 120° C. (Posselger, *Ann. Pharm.* 64, 287.) [W.]

contains an iodide, the iodine must first be precipitated in the form of iodide of copper, by the addition of a copper-salt. (Balard.)

2. The chlorine which serves to separate the bromine is evolved in the mother-liquor itself, after that liquid has been freed as completely as possible by crystallization and other means, from the greater part of the salts which it contains. For this purpose the mother-liquor is heated in a distillatory apparatus, with peroxide of manganese and hydrochloric acid, or when it contains a sufficient quantity of chlorides—with peroxide of manganese and sulphuric acid. The bromine which distils over is afterwards further purified. This method, as being the more economical of the two, is best adapted to the preparation of bromine on the large scale, while the first method is to be preferred for the detection of bromine in analysis.

a. Six parts of the mother-liquor of the *Salins* spring—which contains bromide of magnesium, chloride of sodium, chloride of magnesium, and sulphate of soda—are boiled with milk of lime, containing one part of lime; the filtrate repeatedly evaporated as long as it yields crystals; and the mother-liquor which finally remains, distilled with hydrochloric acid and peroxide of manganese. (Desfosses, *J. Pharm.* 13, 252.) The liquid, after being decomposed by lime, may be treated with sulphate of soda, separated from the gypsum produced, and freed from the greater part of the common salt by crystallization.

b. 240 parts of the mother-liquor of the Schönebeck spring are distilled in a glass retort with 3 parts of peroxide of manganese and 4 parts of oil of vitriol diluted with 2 parts of water—the receiver containing solution of potash. The liquid in the receiver is afterwards evaporated to dryness, and the residual mixture of bromate of potassa with bromide and chloride of potassium, distilled with peroxide of manganese and sulphuric acid; whereupon, the bromine is evolved. Or better: in order first to get rid of the greater part of the hydrochloric acid, the mother-liquor is previously heated with sulphuric acid alone, which expels the hydrochloric acid, but, if carefully managed (that is, by not using too large a quantity, Löwig), scarcely a trace of hydrobromic acid. The sulphates formed are then separated by crystallization, and the remaining liquid distilled with oil of vitriol and peroxide of manganese. (Hermann, *Schw.* 49, 101; *Pogg.* 13, 175; 14, 625.)

c. The mother-liquor of the Kreuznach salt-spring is evaporated in an iron vessel to one-third of its bulk, and, after standing for some days, poured off from the salts which crystallize out. It is then diluted with water—the lime precipitated by means of sulphuric acid—the clear liquid separated from the gypsum by straining and pressing—and then evaporated to dryness, The residue is dissolved in an equal weight of water, whereby a further quantity of gypsum is separated, and lastly, distilled with peroxide of manganese and hydrochloric acid, which may be used in excess without giving rise to the formation of chloride of bromine. (Löwig.) Mohr (*Ann. Pharm.* 22, 66) mixes 4 quarts of the Kreuznach mother-liquor with one ounce of peroxide of manganese and 6 ounces of strong commercial hydrochloric acid in a short-necked flask connected with a long narrow glass tube kept constantly cool, and heats the mixture till the vapours rising in the flask become colourless. A portion of the hydrochloric acid may pass over during the interval—no chlorine is formed because the liquid is not sufficiently concentrated.

d. After the separation of iodine from the mother-liquor of varec by precipitation with chlorine, according to Barruel's process (p. 249), the remaining liquid is distilled with peroxide of manganese and oil of vitriol

(4 parts of peroxide and 3 parts of oil of vitriol to 156 parts of the mother-liquor) in a glass retort, connected, without luting, with a tube-funnel and receiver, and lastly by means of a bent tube, with a glass cylinder. The mixture is boiled till no more red vapours appear; and lastly, the whole of the bromine condensed in the receiver is driven over by a gentle heat into the glass cylinder, which is surrounded by ice-cold water. The residue is tested with peroxide of manganese and sulphuric acid to see if it is free from bromine. (Barruel, Bussy, *J. Pharm.* 23, 19; also *J. pr. Chem.* 13, 251.) Balard proceeds in the same manner, excepting that he passes the bromine vapour into a leaden vessel filled with fragments of iron, and prepares the bromine from the bromide of iron thereby produced. (Lutrand, *J. Pharm.* 23, 184.)

The bromine is generally contaminated with a small quantity of chlorine, which can only be partially removed by washing with a large quantity of water. (Berzelius.)

Properties. Bromine freezes at −19° (Löwig), between −18° and −20° (Serullas), at −25° (Liebig), forming a yellowish-brown, brittle, crystalline, laminated mass, covered with bluish-grey spots. At ordinary temperatures it forms a very mobile liquid of specific gravity 2·966 (Balard); between 2·98 and 2·99 at 15° (Löwig). By reflected light, it appears brownish-red and nearly black; by transmitted light, transparent and of a hyacinth-red colour (Balard); in large quantities, it does not transmit ordinary diffused light; but the light of the sun or of a candle passes through it and exhibits a red colour. (Löwig.) Does not conduct electricity. (Balard, De la Rive Solly.) Volatilizes rapidly in the air, and boils at 47° (Balard), 45° (Löwig), being converted into a yellowish-red vapour, of the same colour as that of hyponitric acid. It has an extremely powerful and offensive odour, resembling that of chloric oxide, which adheres for some days to substances that have been saturated with it. Vapour of bromine when inhaled is less injurious than chlorine gas, and if mixed with a large quantity of air may be breathed with perfect impunity; nevertheless, large quantities give rise to oppression, cough, giddiness, bleeding at the nose, increased secretion of the mucous membrane, and lastly, headache. These symptoms occasionally continue for six hours: they may be alleviated by ammonia and alcohol, but not by sulphuretted hydrogen. (Löwig.) Bromine has a very sharp, burning, astringent, and nauseous taste. (Balard; Löwig.) One drop of bromine administered to a bird through the beak is sufficient to cause death. (Balard.) A small quantity of bromine imparts a transient yellow colour to the skin; a larger quantity produces a yellow, and then a brown colour, which can be removed only with the skin itself, and is attended with violent itching. (Balard, Löwig.) When applied to the skin in still larger quantities, it produces immediate corrosion, and violent inflammation. (Löwig.) Corrodes wood, cork, and other organic substances, imparting a yellow colour to them. (Balard.) Like chlorine, it rapidly discharges the colour of tincture of litmus and indigo without first reddening them. (Balard.) It destroys organic colours. (Löwig.) Colours starch orange-yellow. A burning taper is extinguished in vapour of bromine, but the flame previously appears red at top and green below. (Balard.)

Atomic Weight: 78·4 (Berzelius)—75·76 (Löwig)—75·288 (Liebig)—74·608 to 75·432 (Balard).

Compounds of Bromine.

Bromine and Water.

Hydrate of Bromine. 1. Formed when a mixture of a small quantity of bromine with a large quantity of water is cooled down to the freezing point of water.—2. When bromine vapour is transmitted, at a temperature of + 4° through a glass tube moistened with water. Obtained by the first method, it forms regular octohedrons, of a hyacinth-red colour; by the second, a crystalline scaly mass. When heated above 15°, it is decomposed into bromine, and a supernatant aqueous solution of bromine; at 0°, the two liquids again unite and reproduce the hydrate. (Löwig.)

	Calculation.		Löwig.
Br.	78·4	46·56	45·5
10HO	90·0	53·44	54·5
Br10HO	168·4	100·00	100·0

B. Aqueous Solution of Bromine. *Bromine Water.*—One part of bromine dissolves at 15° in 33·3 parts water. The yellowish-red solution smells like bromine, has a very rough but not acid taste, and remains unchanged even below −20°. It loses bromine when exposed to the air, and still more rapidly when heated, but does not become acid; but when kept for any length of time, especially if exposed to the sun, it acquires acid characters, from formation of hydrobromic acid. (Löwig.)

Bromine and Oxygen.

Bromine, like iodine and chlorine, cannot be made to unite directly with oxygen.

A. Hypobromous Acid. BrO?

The similarity of bromine to chlorine in its behaviour towards salifiable bases renders it highly probable that it forms a hypobromous acid BrO,—analogous to hypochlorous acid, ClO—which, in union with salifiable bases, forms compounds characterized by their bleaching action on organic colours. Such bleaching liquids are formed when bromine is added to the solution of a fixed alkali in excess, the alkali being either caustic or combined with carbonic or some other weak acid. Under these circumstances little or no bromate is formed, and the solution may be supposed to contain a metallic bromide and an alkaline hypobromite together with free alkali.

$$2KO + 2Br = KBr + KO, BrO.$$

These solutions do not smell of bromine, but have an odour similar to that of the bleaching liquids of chlorine: they decolorize litmus and indigo; disengage nitrogen from ammonia, and evolve bromine with all acids, even with carbonic acid.

$$KBr + KO, BrO + 2SO^3 = 2(KO, SO^3) + 2Br.$$

When heated or mixed with an excess of bromine, they lose their bleaching properties, because the hypobromite is thereby resolved into metallic bromide and bromate.

$$3(KO, BrO) = 2KBr + KOBrO^5.$$

In the case of lime only, an excess of bromine does not alter the bleaching compound. With protoxide of mercury bromine-water produces a sparingly soluble compound of bromide and oxide of mercury, together with a liquid containing hypobromite of mercury or free hypobromous acid, and yielding the latter by distillation in vacuo. (Balard.) According to Gay-Lussac (*Compt. Rend.* 14, 951), hypobromous acid may be prepared in the gaseous form, by means of protoxide of mercury in the same manner as hypochlorous acid. (*Vid.* also Fritzsche, *J. pr. Chem.* 24, 291.)

B. Bromic Acid. BrO^5.

Bromsäure, Acide Bromique. — *Formation.* 1. Bromine-water with hypochlorous acid forms bromic acid and free chlorine.—2. With oxide of gold, it yields bromate and bromide of gold. When mixed in excess with solutions of the fixed alkalis, it forms, in the same manner as iodine and chlorine, 5 atoms of metallic bromide (or alkaline hydrobromate) and one atom of alkaline bromate.—3. Pentachloride of bromine is resolved by contact with alkalis into metallic chloride (or hydrochlorate) and a salt of bromic acid. (Balard.)

Bromine is not oxidized by chloric oxide, chloric acid, or concentrated nitric acid. (Balard, Connell, *N. Ed. Phil. J.* 13, 283.)

Not yet known in the free state.

	Calculation.		Balard.
Br	78·4	66·21	64·69
5O	40·0	33·79	35·31
BrO^5	118·4	100·00	100·00

($Br^2O^5 = 2 . 489·17 + 5 . 100 = 1478·3$. Berzelius.)

Combinations. a. *Aqueous Bromic Acid.*

Preparation. 1. An aqueous solution of bromate of baryta is precipitated by an equivalent quantity of sulphuric acid, and the filtrate gently evaporated to a small bulk. (Balard.) Rammelsberg digests 100 parts of bromate of baryta with 240 parts of water, and 24 parts of oil of vitriol, for a long time, frequently agitating the liquid, and applying only a very gentle heat, because a more elevated temperature partially decomposes the bromic acid. A small quantity of bromate of baryta invariably remains undecomposed; whence it is necessary to precipitate the sulphuric acid still remaining in the solution by a quantity of baryta water just sufficient for the purpose, and afterwards to decant the liquid, as filtering-paper would colour it yellow. In order not to lose the bromate of baryta which remains undecomposed, it is digested with a fresh quantity of dilute sulphuric acid; the decanted liquid saturated with carbonate of lime, and concentrated by evaporation; and the bromate of lime contained in the decanted solution converted into bromate of potash by precipitation with carbonate of potash.—2. Boiling water is saturated with bromate of potassa, and an excess of hydrofluosilicic acid added; the mixture is then heated for a short time—filtered—and bromate of potash added to the filtrate as long as the salt continues to be converted into a gelatinous mass; the excess of bromate of potash is then thrown down by alcohol, and the filtrate left to evaporate at a gentle heat. (Löwig.) Alcohol cannot be used in the preparation, inasmuch as it is violently decomposed by contact with the bromic acid, and converted into acetic acid. (Serullas;

Rammelsberg.) Hence the bromate of potash must be mixed hot with excess of hydrofluosilicic acid, filtered on cooling, the solution gently evaporated, and after a few days, filtered once more through pounded glass. (Serullas.) The excess of hydrofluosilicic acid cannot, however, be completely got rid of, even by evaporating the solution with silica. (Rammelsberg.)

Colourless liquid, of a syrupy consistence after sufficient concentration; nearly inodorous; of a very acid but not caustic taste; reddens litmus strongly, and bleaches it after a time. (Balard.) Of a reddish colour; cannot be reduced to a syrupy consistence; has a peculiar characteristic odour; reddens litmus, and then rapidly decolorizes it. (Serullas.)

The acid volatilizes both on exposure to heat and in vacuo, part remaining undecomposed, the rest being resolved into bromine vapour and oxygen gas. (Balard.) It is decomposed, even at 100° into vapour of bromine and oxygen, without the evolution of any portion of undecomposed acid. (Rammelsberg.) Not decomposed by nitric or sulphuric acid, excepting that the oil of vitriol—in consequence of the heat disengaged—may evolve a small quantity of bromine vapour and oxygen gas, with effervescence. Bromic acid and sulphurous acid decompose each other, yielding bromine and sulphuric acid: with hydrosulphuric acid the products are—water, bromine, and sulphur; with hydriodic acid, water and bromide of iodine; with hydrobromic acid, water and bromine; with hydrochloric acid, water and chloride of bromine. The salts of these acids behave in a similar manner. (Balard.) Alcohol and ether rapidly decompose bromic acid, with rise of temperature and formation of acetic acid. (Serullas.) Aqueous bromic acid added to concentrated solutions of lead produces a white precipitate, which dissolves on the addition of a larger quantity of water; it also gives white precipitates with dilute solutions of mercurous and silver-salts. (Balard.)

b. *The Salts of Bromic acid, Bromates*, are obtained: 1. By directly combining the salifiable bases with aqueous bromic acid.—2. Bromine is added to the aqueous solution of a fixed alkali, as long as its colour disappears, and the more sparingly soluble bromate is separated from the metallic bromide (or alkaline hydrobromate) by crystallization.—3. Chloride of bromine is dissolved in the aqueous solution of a fixed alkali, and the alkaline bromate separated from the metallic chloride (or alkaline hydrochlorate) by crystallization.—4. Bromine is placed in contact with oxide of gold (p. 277).

The bromates, when heated to redness, either evolve 6 atoms of oxygen and leave metallic bromides (as is the case with the bromates of potassa, soda, mercury, and silver); or they give off 5 atoms of oxygen and 1 atom of bromine vapour, leaving metallic oxides (as with the salts of magnesia, alumina, and zinc). They explode—either by heat or by percussion—with charcoal, sulphur, antimony, and other combustible bodies, the report being as loud as with the chlorates. The mixture of a bromate with a combustible substance is sometimes inflamed by oil of vitriol. (Löwig.) When treated with oil of vitriol alone, they give off bromine and oxygen. (Löwig.) They are likewise decomposed by dilute phosphoric, sulphuric, nitric, oxalic, and acetic acid, aided by very gentle heat, oxygen gas being evolved and bromine set free. (Balard; Löwig.) Their aqueous solutions are decomposed at ordinary temperatures—with separation of bromine—by sulphurous acid, hydrosulphuric acid (sulphur in this case being deposited, and sulphuric acid formed—*H. Rose*), and hydrobromic acid. (Balard.) Hydrochloric acid added to a bromate forms a metallic chloride and chloride of bromine. (Balard.) Arsenious acid

does not decompose these salts. (Simon.) They are for the most part soluble in water. Their aqueous solutions give, with mercurous salts, a yellowish-white precipitate, soluble in nitric acid; with silver-salts a white precipitate, which scarcely blackens when exposed to light, and is readily soluble in ammonia, but not in dilute nitric acid; a concentrated solution likewise gives a white precipitate with lead-salts. (Balard; Löwig.)

The preparation of *Perbromic acid*, BrO^7, was tried by Rammelsberg in various ways, but failed in every instance.

Bromine and Hydrogen.

A. Hydrobromous Acid.

Hydrobromige Säure, Acide hydrobromique bromé. Known only in the state of aqueous solution and in combination with a few salifiable bases. An aqueous solution of hydrobromic acid dissolves bromine, forming a dark-red solution, which again evolves the bromine when heated or exposed to the air. (Balard.) The alkaline bromides or hydrobromates when dissolved in water take up a quantity of bromine equal to that which they already contain, and form dark-red solutions which, on exposure to heat, give off the excess of bromine in the form of vapour. (Löwig.)

B. Hydrobromic Acid. HBr.

Hydrobrom, Hydrobromsäure, Bromwasserstoffsäure, Hydrobrom-Gas, Acide hydrobromique.

Formation. 1. Bromine does not combine with hydrogen gas at ordinary temperatures, even when exposed to direct sunshine; but if a red-hot iron wire is introduced into hydrogen gas saturated with bromine vapour, hydrobromic acid is formed round the wire, though not throughout the whole mass. (Balard.)—2. Bromine by itself does not decompose water, when passed, together with aqueous vapour, through a red-hot tube. (Balard.) But if the bromine is in excess and the porcelain tube heated nearly to whiteness, a tolerably large quantity of oxygen gas and hydrobromic acid is obtained; and if the aqueous vapour predominates, a colourless gas is the result, which smells like garlic, burns with a purplish-red flame, and is not absorbed by water or potash (?). (Bourson, *Compt. Rend.* 13, 1154; also *Pogg.* 55, 88; also *J. pr. Chem.* 25, 400.) Under the direct influence of the sun's rays, bromine gradually separates oxygen gas from water, and forms hydrobromic acid. (Löwig.) When the mixture is brought in contact with substances which have an affinity for the oxygen of the water, such as phosphorus, hypophosphorous acid, sulphurous acid, arsenious acid, metals, &c., hydrobromic acid is instantly produced. (Balard.) Moreover, on boiling bromine with fuming nitric acid, a small quantity of hydrobromic acid is evolved, in consequence of the hyponitric acid being converted by the oxygen of the water into nitric acid. (Connell, *N. Ed. Phil. J.* 13, 283.)—3. Bromine separates hydrogen from most other hydrogen compounds, namely, from phosphuretted hydrogen gas, gaseous or aqueous hydrosulphuric and hydriodic

acids, and aqueous ammonia. It is also very rapidly converted into hydrobromic acids by volatile oils and resins, by alcohol and ether in the course of a few days, and by fixed oils and vinegar after a longer interval. (Balard.)

Preparation. 1. Bromine is made to combine with phosphorus, and the compound heated in a retort with a very small quantity of water. (Balard.)—2. Millon (*J. Pharm.* 28, 299) heats a mixture of one part of phosphorus, 12·5 parts of bromine and 7·8 parts of bromide of potassium with a small quantity of water. [For the method of proceeding and the calculation, *vid.* p. 262, under the head of *Hydriodic acid.*]—3. Bromide of potassium is heated with three-fourths of its weight (Löwig) of oil of vitriol. In this process the gas is very apt to be contaminated with vapour of bromine, (which may be separated by agitation with mercury), and with sulphurous acid; the quantity of these impurities is, however, less in proportion as the crystals of bromide of potassium are larger, and the excess of oil of vitriol employed is smaller. (Balard.) The gas is received over mercury.

Properties. Colourless gas, having a very pungent odour, which excites coughing, and a strongly acid taste; reddens litmus strongly, and excites itching and inflammation when applied to the skin. Fumes in the air more strongly than hydrochloric acid. (Balard.) Specific gravity (I, 279); according to Löwig, it is 2·71.—Liquefies at − 92° F.; solidifies at −100° F.

	Calculation.			Vol.	Sp. gr.
Br	78·4	98·74	Bromine vapour	½	2·71775
H	1·0	1·26	Hydrogen gas	½	0·03465
HBr	79·4	100·00	Hydrobromic acid gas	1	2·75240

HBr = 6·24 + 484·15 = 495·39. (Berzelius.)

Decompositions. Hydrobromic acid gas is not decomposed when transmitted, either alone or mixed with oxygen gas, through a red-hot glass tube; or when a burning taper is introduced into the mixture. 1. Oil of vitriol and aqueous hydrobromic acid react on each other but slightly, yielding small quantities of sulphurous acid, water, and bromine; with nitric acid, the decomposition is slow at first, but afterwards becomes more rapid—especially if heat is applied to the mixture: the products are hyponitric acid, water, and bromine (a case of reciprocal affinity, *vide* p. 279, 2). Bromic acid and hydrobromic acid act upon each other in such a manner as to form water and bromine.—2. Chlorine mixed with hydrobromic acid gas forms hydrochloric acid, and separates the bromine in red vapours, which condense in drops; if the chlorine is in excess, chloride of bromine is produced.—3. Potassium separates the bromine from hydrobromic acid gas at ordinary temperatures; tin, with the aid of gentle heat, leaving half a measure of hydrogen. Mercury has no effect on the gas.—4. The oxides of lead and silver decompose the gas at ordinary temperatures into metallic bromide and water; most of the other salifiable metallic oxides effect this change when heated.—5. Metallic acids and peroxides, such as antimonic acid, peroxide of manganese, and the red and brown peroxides of lead, undergo mutual decomposition with aqueous hydrobromic acid, yielding bromide of the metal (or hydrobromate of the oxide) and free bromine. (Balard.)

Combinations.—a. *Aqueous Hydrobromic acid, Solution of hydrobromic acid.*—1. Hydrobromic acid gas is rapidly and copiously absorbed by water, with disengagement of heat (Balard); and by ice, which is thereby liquefied. (Löwig.)—2. Bromine is added to phosphorus immersed in water, in small quantities at a time, to avoid too violent a disengagement of heat. The addition of the bromine is continued till the whole of the phosphorus has disappeared; after which, the aqueous hydrobromic acid is obtained pure by distillation. (Löwig.)—3. Bromide of antimony is decomposed by a sufficient quantity of water to prevent any antimonic oxide from being dissolved. (Serullas.) Antimony always remains in the solution. (Löwig.)—4. Sulphuretted hydrogen gas is passed through water containing a little bromine—small quantities of that substance repeatedly added to the liquid as often as the hydrosulphuric acid is in excess—and the solution filtered from the precipitated sulphur. (Balard.) In this process, bromide of sulphur is formed, which volatilizes in dense fumes and is decomposed by water into hydrobromic acid and sulphurous acid. (Löwig.)—5. One part of bromide of potassium is distilled with $\frac{3}{4}$ pt. of oil of vitriol and 12 pts. of water, and the distillate freed from excess of bromine by exposure to the air. (Löwig.)—6. Bromide of barium dissolved in water is decomposed by an equivalent quantity of dilute sulphuric acid, and the solution filtered. (Glover, *Phil. Mag. J.* 19, 92.)

Aqueous hydrobromic acid is colourless; in the most concentrated form it has a specific gravity of 1·29 (Löwig), and fumes in the air; has a strongly acid taste. (Balard.) The strongest acid boils at a temperature below 100°, and is thereby rendered weaker, owing to the loss of hydrobromic acid gas; a more dilute acid boils at a temperature above 100°, and a very dilute acid becomes stronger on boiling. (Löwig.) The aqueous acid undergoes the same decompositions as hydrobromic acid gas, as described under the numbers 1, 2, 4, and 5. When mixed with nitric acid, it dissolves gold and platinum. (Balard.)

b. *Hydrobromates.* Vide *Bromides.*

¶ BROMINE AND BORON.

BROMO-BORACIC ACID.

When vapour of bromine is passed over an ignited mixture of vitrefied boracic acid and charcoal, a colourless gas is obtained, which has a very penetrating odour and extremely acid taste, reddens litmus strongly, and forms white fumes in contact with moist air. It appears to be composed of BBr^3. It is rapidly absorbed by water, but is, at the same time, decomposed, with separation of boracic acid. When brought in contact with dry ammoniacal gas, it forms a white, volatile, pulverulent salt, which has a pungent taste, and is resolved by contact with water into bromine and borate of ammonia. (Poggiale, *Compt. Rend.* 22, 124.) ¶

BROMINE AND PHOSPHORUS.

A. BROMIDE OF PHOSPHORUS. When phosphorus is brought in contact with bromine contained in a vessel full of carbonic acid gas, combination takes place instantaneously, and with incandescence, the product being sometimes terbromide, sometimes pentabromide of phosphorus. (Balard.) Small fragments of phosphorus thrown into bromine take fire and produce dangerous explosions. (H. Rose, *Pogg.* 27, 128.)

a. *Terbromide of Phosphorus. Protobromure de Phosphore.* 1. Phosphorus is added in pieces, not weighing more than a quarter of a grain, to perfectly anhydrous bromine, till the liquid becomes colourless, after which the compound is separated by distillation from the excess of phosphorus. (Löwig.) In order to avoid the chance of explosion, it is best to pour the bromine into a wide-mouthed bottle, and introduce perfectly dry phosphorus in a glass tube, sealed at bottom, and placed upright in the liquid; so that on closing the bottle, the bromine vapour may slowly come in contact with the phosphorus. (H. Rose, *Pogg.* 28, 550.)—2. Vapour of phosphorus is passed over protobromide or dibromide of mercury, which is heated in a glass tube by means of a spirit-lamp, and the product collected in a cooled receiver; the new compound is purified from excess of phosphorus by distillation. (Löwig.)

Colourless, transparent, mobile liquid, which does not freeze even at − 12°, is very volatile, and emits dense white fumes in the air; has the pungent odour of hydrobromic acid; it probably reddens litmus paper only when moisture is present. (Löwig; Balard.)

	Calculation.		Löwig.		Volume.
P	31·4	11·78	11·7	Vapour of phosphorus	1
3Br	235·2	88·22	88·3	Vapour of bromine	6
PBr^3	266·6	100·00	100·0		

Decompositions. 1. By water, with great disengagement of heat, into phosphorous acid and hydrobromic acid, which latter, when a small quantity only of water is employed, is evolved in the gaseous form. (Balard.) At + 8°, the decomposition takes place but slowly, even when the mixture is repeatedly shaken; at 25° it proceeds very rapidly. (Löwig.) 2. By chlorine, into chloride of phosphorus and free bromine. (Balard.)

Terbromide of phosphorus is capable of dissolving an additional quantity of phosphorus, whereby it acquires the property of setting fire to combustible bodies brought in contact with it in the open air (Balard), of forming a pellicle of phosphorus when exposed to air, and depositing phosphorus when decomposed with water. (Löwig.)

b. *Pentabromide of Phosphorus. Perbromure de Phosphore.*—1. Sublimes on bringing bromine in contact with phosphorus, not in very great excess. (Balard.)—2. Formed by mixing terbromide of phosphorus with bromine. (Löwig.)—3. Bromine decomposes iodide of phosphorus. (Balard.)

Lemon-yellow solid, which crystallizes in the rhombohedral form after fusion, in needles when sublimed. Melts at a moderate heat to a red liquid, which at a higher temperature evolves red vapours; evolves dense pungent fumes in the air. (Balard.)

	Calculation.		Löwig.		Volume.
P	31·4	7·42	6·8	Vapour of phosphorus	1
5Br	392·0	92·58	93·2	Vapour of bromine	10
PBr^5	423·4	100·00	100·0		

Decompositions. 1. By chlorine, into chloride of phosphorus and free bromine.—2. By heated metals into metallic bromide and phosphide. (Balard.)—3. By oxide of copper and red oxide of mercury into metallic bromide and phosphate of the oxide. (Löwig.)—4. By water, with rise of temperature, into phosphoric and hydrobromic acids. (Balard.)

B. Hydrobromate of Phosphuretted Hydrogen. 1. Formed when dry phosphuretted hydrogen and hydrobromic acid gases are brought in contact with each other.—2. Bromide of silicium is introduced under a bell-jar full of phosphuretted hydrogen gas, and a small quantity of water added, whereby the bromide of silicium is converted into silica and hydrobromic acid gas. The compound crystallizes on the sides of the vessel. (Serullas.)

Colourless cubes, sometimes transparent, sometimes opaque. (Serullas.) Boiling point about 30°; specific gravity of the vapour = 1·906. (Bineau, *Ann. Chim. Phys.* 68, 430.)

When exposed to the air it absorbs moisture; and when treated with water, it is resolved, with violent ebullition, into aqueous hydrobromic acid and non-spontaneously inflammable phosphuretted hydrogen gas. (Serullas.)

Calculation.				Vol.	Sp. gr.
PH	34·4	30·23	Phosphuretted hydrogen gas	½	0·5962
HBr	79·4	69·77	Hydrobromic acid gas	½	1·3762
PH^3,HBr	113·8	100·00	Hydrobromate of phosphuretted hydrogen vapour	1	1·9724

Bromine and Sulphur.

A. Bromide of Sulphur. Sulphur dissolves in bromine without any observable rise of temperature (H. Rose), forming a brownish-red oily liquid, lighter than bromine, darker than chloride of sulphur. This compound, when exposed to the air, evolves white fumes, which smell like chloride of sulphur; it reddens dry litmus-paper very feebly, but moistened litmus-paper strongly. It is but very slowly decomposed by cold water: at a boiling heat, however, the decomposition is frequently attended with slight explosion, the products being hydrobromic, hydrosulphuric, and sulphurous acids. Chlorine converts it into chloride of sulphur and free bromine. (Balard.)

At ordinary temperatures, 75 parts (one atom) of bromine dissolve 32 parts (2 atoms) of sulphur; and when aided by heat, a larger quantity, which, however, separates again on cooling. The solution is decomposed by water, and more rapidly when the mixture is shaken, into hydrobromic acid, sulphur, and sulphurous acid. When it is distilled with phosphorus, bromide of phosphorus passes over, and sulphur is left in the retort. When it is distilled alone, half the sulphur remains behind, and the distillate consists of monobromide of sulphur. This compound is red, heavier than water, very volatile, and, on exposure to the air, emits the same vapour as the dibromide of sulphur, with a similar odour; it has a sharp, acid, burning taste, and does not redden dry litmus-paper. It is decomposed by water in a similar manner to the dibromide. Nitric acid attacks it violently, converting it into hydrobromic acid and sulphuric acid. With ammonia, it yields sulphur, nitrogen gas, and hydrobromate of ammonia. When passed in the form of vapour over ignited iron, it produces bromide and sulphide of iron, with disengagement of light and heat. (Löwig.)

Bromine does not appear to form definite compounds with sulphur. If a saturated solution of sulphur in bromine, prepared at ordinary temperatures, is partially distilled at a very gentle heat, the distillate, which

is of as deep a red colour as bromine, has the composition *b*; the residue again distilled at a somewhat higher temperature, but still far below its boiling point, yields the distillate *c*; and sulphur, rendered darker by the presence of bromine, remains in the retort. On distilling this residue, a dirty brown liquid *a*, is obtained. Again, if the distillate *c* is exposed to a gentle but gradually increasing heat,—the temperature however being always kept below the boiling point and the receivers thrice changed during the process,—the distillate *f* passes over first and then the distillate *e*, both resembling bromine in colour,—and lastly the distillate *g*, which is somewhat yellower; the residue in the retort consists of dirty brown sulphur containing bromine. (H. Rose.)

	a,	*b*,	*c*,	*d*,	*e*,	*f*.
S	89·57	78·01	74·42	27·59	15·02	9·38
Br	10·43	21·99	25·58	72·41	84·98	90·62
SBr.	100·00	100·00	100·00	100·00	100·00	100·00

B. *Sulphate of Bromide of sulphur?* A solution of sulphur in bromine—in which the quantity of sulphur present is not sufficient to render it less fluid than bromine itself,—absorbs the vapour of anhydrous sulphuric acid in abundance, without undergoing any change of appearance. On distilling the mixture, no sulphurous acid is evolved, but sulphur is left behind. The distillate first obtained is reddish-brown, fuming, and readily soluble in water. The aqueous solution, which is coloured yellow by free bromine, likewise contains hydrobromic and sulphuric acids. The distillate obtained at a subsequent period is reddish-brown, and dissolves very slowly in water, with separation of sulphur. The solution contains hydrobromic and sulphuric acids, but no free bromine. (H. Rose, *Pogg.* 44, 1, 327.)

C. Sulphate of Hydrobromic acid? Anhydrous sulphuric acid absorbs hydrobromic acid gas and deliquesces to a red liquid. (Aimé, *J. Pharm.* 21, 88.)

D. Bromide of sulphide of Carbon. Bromine dissolves with great readiness in bisulphide of carbon, by which it is separated from solution in water. (Lampadius, *Schw.* 50, 378.) The red solution is heavier than water, has a peculiar odour, both of bromine and of bisulphide of carbon, and moreover very pungent; it gives up its bromine to aqueous solutions of the alkalis, but not to pure water. (Löwig.) Does not conduct electricity. (Solly.)

Bromine and Selenium.

Bromide of Selenium. The two elements are miscible in various proportions; but the compound containing 5 parts of bromine and one part of selenium appears to be the most stable. Bromine rapidly combines with powdered selenium, the combination being attended with a hissing noise and strong disengagement of heat; the mixture instantly solidifies to a brownish-red mass, interspersed with portions of a yellow colour. When exposed to the air, it emits fumes which have exactly the odour of chloride of sulphur. The compound volatilizes when heated, part being decomposed into bromine and selenium, and the rest sublimed, without decomposition, in the form of a yellow mass. It dissolves completely in water, with the exception of a few flakes of selenium. The

colourless solution contains hydrobromic and selenious acids, and on the addition of hydrochloric acid gives a precipitate of selenium [which appears difficult of explanation]. (Serullas.)

Bromine and Iodine.

A. Sub-bromide of Iodine. Formed when iodine is brought in contact with a small quantity of bromine. Solid; volatilizing in reddish-brown vapours, which condense to reddish-brown crystals, collected together in fern-like masses. (Balard.)

B. Pentabromide of Iodine. Iodine forms with excess of bromine a dark-brown liquid (Balard), having an offensive odour and astringent taste. (Löwig.) It dissolves pretty freely in water, with separation of iodine or bromine, according as either may be in excess. (Löwig.) The brownish-red solution contains undecomposed bromine of iodine; hence it decolorizes litmus without previously reddening it. With alkalis, it yields a metallic bromide (or hydrobromate) and an alkaline iodate. (Balard.) It is also decolorized by exposure to the sun's rays, in consequence of the formation of hydrobromic and iodic acids. (Löwig.)

Hydrated Pentabromide of iodine. A mixture of bromide of iodine with a small quantity of water is exposed to a temperature below 0°. Brownish-yellow needles, frequently united in arborescent masses. At a temperature above + 4°, it is resolved into bromide of iodine and water, which contains a small quantity of bromide of iodine dissolved: on exposure to cold, the two strata of liquid again unite and reproduce the hydrate. (Löwig.)

Other Compounds of Bromine.

A. With Chlorine.—B. With metals, forming the *Metallic Bromides.* These compounds are obtained: 1. When bromine is brought in contact with a metal. Potassium, arsenic, antimony, and tin combine directly with liquid bromine, producing vivid combustion; potassium even produces explosion. Bismuth, iron, and mercury combine with bromine at ordinary temperatures without combustion; but if heat be applied, combustion takes place. Gold combines gradually with bromine at ordinary temperatures; platinum does not. (Balard; Löwig.) With many metals, the application of heat is necessary to induce combination. (Berthemot.) —2. Many metals abstract bromine from hydrobromic acid gas (p. 288). Vapour of bromine passed over ignited potassa, soda, baryta, or lime, forms a metallic bromide, the action being attended with development of light and heat and evolution of oxygen gas: from alkaline carbonates bromine immediately expels the carbonic acid; oxide of silver is decomposed by it, even at ordinary temperatures. On the other hand, it does not decompose the sulphates of potassa, magnesia, zirconia, or oxide of zinc, even with the aid of heat. (Balard.)—4. Metallic oxides brought in contact with hydrobromic acid produce metallic bromides and water, the decomposition taking place, sometimes at ordinary, sometimes at higher temperatures.

The metallic bromides are solid at ordinary temperatures; most of them fuse at a moderate heat, and volatilize at higher temperatures. They closely resemble the chlorides. But few metallic bromides (gold, platinum) give up their bromine by mere exposure to heat; many of them,

however, when ignited under such circumstances that the air has free access to them, give off vapour of bromine, and are converted into oxides. (Berthemot.) Chlorine, with the aid of heat, drives out the bromine and converts them into chlorides. Hydrochloric acid gas decomposes them at a red heat, forming a metallic chloride and hydrobromic acid gas, equal in volume to the hydrochloric acid. Anhydrous boracic acid does not decompose bromide of potassium at a red heat; but if water has access to the mixture, borate of potassa and hydrobromic acid gas are produced. Concentrated sulphuric or nitric acid separates bromine from metallic bromides, with formation of sulphurous acid or nitrous gas, sometimes accompanied with hydrobromic acid. (Balard.) When fused with sulphate of potassa, the metallic bromides evolve sulphurous acid and bromine. When added to a bead of microcosmic salt saturated with oxide of copper, they impart a blue colour to the blow-pipe flame, similar to that produced by a chloride under the same circumstances; but the colour inclines more to green. (Berzelius.) Pure metallic bromides distilled with chromate of potassa and oil of vitriol, yield pure bromine, which loses its colour when treated with aqueous ammonia; but if a chloride is mixed with the bromide, chromate of terchloride of chromium likewise passes over, and forms a yellow liquid when mixed with the ammonia. (H. Rose, *Analyt. Chem.* 1, 415.) A few metallic bromides remain unaltered in contact with water; viz. dibromide of copper, dibromide of mercury, and bromide of silver. A few others are converted into metallic oxides and hydrobromic acid, which dissolves in the water; but the decomposition generally takes place in such a manner that the metallic oxide retains a portion of bromide, and the hydrobromic acid dissolves a portion of the oxide produced (this is the case with the bromides of arsenic, antimony, tellurium, and bismuth). Most metallic bromides dissolve completely in water, forming solutions which may be regarded as containing either metallic bromides or hydrobromates of metallic oxides.

Hydrated Metallic Bromides, or *Hydrobromates of Metallic Oxides, Hydrobromates, Bromhydrates.—Preparation.* 1. By dissolving a metallic bromide in water, or bringing bromine and a metal in contact with water. 2. By the direct combination of a base with aqueous hydrobromic acid. 3. By dissolving certain metals in aqueous hydrobromic acid, the action being attended with evolution of hydrogen gas, proceeding either from the acid or from the water: thus

$$Zn + HBr = ZnBr + H$$
$$\text{or: } Zn + HBr + HO = ZnO, Br + H.$$

The aqueous solutions of the bromides of calcium, magnesium, manganese, and zinc exert an alkaline reaction. (Bonsdorff.) Hydrobromates are often resolved by evaporation to dryness and subsequent exposure to a higher temperature,—sometimes even by crystallization—into metallic bromides and water; but some of them, as those of the earths, evolve hydrobromic acid together with the aqueous vapour, which escapes, and leave metallic oxides. Chlorine added to an aqueous solution of one or these salts sets bromine free and forms a chloride or hydrochlorate:

$$KBr + Cl = KCl + Br; \text{ or, } KO, HBr + Cl = KO, HCl + Br.$$

Hence chlorine water or chlorine gas colours the solutions yellow or yellowish-red (without destroying the colour if added in excess); and on subsequently agitating the liquid with ether, a reddish-yellow solution of bromine in ether is obtained, which floats on the surface of the nearly decolorized watery liquid; the liberated bromine also communicates an

orange-yellow colour to solid or gelatinous starch. One part of bromide of potassium dissolved in 1000 parts of water communicates in this manner an orange tint to ether or gelatinous starch; $\frac{1}{2}$ pt. colours ether very feebly, and starch pale orange; $\frac{1}{4}$ pt. no longer colours ether, and gives merely a pale yellowish tint to gelatinous starch. If the bromide of potassium is mixed with iodide, the yellow colour caused by the bromine is completely masked by the blue produced by the iodine. (Brandes, *Schw.* 58, 482.) An aqueous solution of a bromide mixed with sulphate of copper produces a black spot on polished silver. (Berzelius.) Salts of hypochlorous acid—chloride of lime, for example—also liberate bromine from these solutions; so likewise do oil of vitriol, chloric acid, and nitric acid. (Balard.) Dilute sulphuric acid generally separates undecomposed hydrobromic acid, which may be obtained by distillation. (Löwig.) The salts of hydrobromic acid give a white precipitate with lead-salts, and yellowish-white with mercurous and silver-salts. The precipitate of bromide of lead does not dissolve on the addition of a large quantity of water (this distinguishes it from the chloride), and the precipitate of bromide of silver is insoluble in dilute nitric acid: it is also insoluble in ammonia, unless the ammonia be strong. (Löwig.) A solution of bromide of potassium containing one part of bromine in 25,000 of water gives a cloud and precipitate with nitrate of mercurous oxide; with nitrate of silver only a very slight cloud; with 100,000 parts of water, the mercurous salt still gives a perceptible turbidity,—the silver-salt, a scarcely visible cloud after some time; with 200,000 parts of water the mercurous salt gives, after a while, a slight opalescence, but the silver-salt has no effect. (Lassaigne, *J. Chim. Méd.* 8, 520.)

Metallic bromides sometimes combine with the oxides of the corresponding metals, forming compounds called *Oxy-bromides*. These compounds, however, still retain water, even after drying at high temperatures, and may be regarded either as compounds of hydrated metallic bromides with metallic oxides, or of hydrobromates of metallic oxides with excess of oxide (arsenic, antimony, bismuth).

Many metallic bromides combine with ammonia in definite proportions.

Electro-negative metallic bromides combine with electro-positive compounds of the same order, forming the *Bromine-salts* of Bonsdorff.

C. **With Organic Substances**: as alcohol, ether, camphor, starch. Bromine is also a constituent of certain artificial organic compounds.

CHAPTER X.

CHLORINE.

Chlorine in general.

Scheele. *Opusc.* 1, 247.
Westrumb. *Crell. Ann.* 1790, 1, 3.
Berthollet. *Mem. de l'Acad. d. Sc. à Paris*, 1785, 276; also *Crell. Chem. Ann.* 1790, 2, 444.—*Ann. Chim.* 80, 54; also *Gilb.* 42, 299.
Chenevix. *Nicholson's J. of Nat. Phil.* 1802, 171 and 229; also *A. Gehl.* 1, 583; abstr. *Gilb.* 12, 416.
Sir Humphry Davy. Phil. Trans.; 1809, I; 91, 1810, II, 231; and 1811, I. 1; also *Schw.* 3, 79, 93, 95, 205, and 256; also *Gilb.* 35, 460; 36, 188; 39, 3, 43, and 90. Further: *Gilb.* 45, 117.
Gay-Lussac & Thénard. *Recherches*, 2, 93.—*Mém. d'Arcueil*, 2, 357; abstr. *Gilb.* 35, 8.
Gay-Lussac. *Ann. Chim.* 91, 96; also *Schw.* 14, 79.
Berzelius. *Gilb.* 37, 458; 38, 217 and 227; 42, 288 and 299.
Friedr. Graf von Stadion. *Oxide of Chlorine and Perchloric acid. Gilb.* 52, 197 and 339.
H. Davy & Faraday, *Liquid Chlorine. Phil. Trans.* 1823, 160 and 198; also *Ann. Phil.* 5, 304 and 393; also *Kastn. Arch.* 1, 89; abstr. *Schw.* 38, 116.
Faraday. *Hydrate of Chlorine. Qu. J. of Sc.* 15, 71; also *Kastn. Arch.* 1, 89; abstr. *Schw.* 38, 116 and 301.
Hypochlorous Acid and *Bleaching Salts.* Berthollet. *Stat. Chim.* 2, 183; also *A. Gehl.* 1, 631.—Wagenmann. *Gilb.* 35, 115.—Geiger. *Repert.* 15, 40.—*Mag. Pharm.* 8, 79.—Robiquet. *J. Pharm.* 10, 93.—Grouvelle. *Ann. Chim. Phys.* 17, 37; also *Schw.* 33, 428.—Berzelius. *Pogg.* 12, 529.—Liebig. *Pogg.* 15, 441.—Soubeiran. *Ann. Chim. Phys.* 48, 113; also *J. Pharm.* 17, 657; 18, 1; also *Ann. Pharm.* 1, 257.—Balard. *Ann. Chim. Phys.* 57, 225; abstr. *Ann. Pharm.* 14, 167 and 298; abstr. *J. pr. Chem.* 4, 152.—Martens. *Ann. Chim. Phys.* 61, 193; also *J. pr. Chem.* 8, 264.—Gay-Lussac. *Compt. Rend.* 14, 927.—Detmer. *Ann. Pharm.* 38, 31.
Oxide of Chlorine. Count Stadion (vid. *sup.*)—H. Davy. *Phil. Trans.* 1815, 214; also *Ann. Chim. Phys.* 1, 76.—Gay-Lussac. *Ann. Chim. Phys.* 8, 408.
Chloric Acid. Vauquelin. *Ann. Chim.* 95, 91; also *Gilb.* 52, 295; also *N. Tr.* 1, 1, 242; 1, 2, 268.—Serullas. *Ann. Chim. Phys.* 45, 204 and 270.
Perchloric Acid. Count Stadion (vid. *sup.*)—Serullas. *Ann. Chim. Phys.* 45, 270; also *J. Chim. Med.* 7, 97; also *Pogg.* 21, 164.—*Ann. Chim. Phys.* 46, 294, 297 and 323; also *Pogg.* 22, 289.—Mitscherlich. *Pogg.* 25, 298.
Compounds of Chlorine and Oxygen. Millon. *N. Ann. Chim. Phys.* 7, 298; also *Ann. Pharm.* 46, 281.
Hydrochloric Acid. Will. Henry. *Phil. Trans.* 1800, 188; also *Scher. J.* 5, 439; abstr. *Gilb.* 7, 265. *Phil. Trans.* 1812, 238; also *Gilb.* 47, 237.

Phosgene; J. Davy, *Phil. Trans.* 1812, 144; also *Schw.* 3, 429; 9, 199; also *Gilb.* 40, 220; 43, 296.

Chloride of Boron; Berzelius, *Pogg.* 2, 147.—Dumas, *Ann. Chim. Phys.* 31, 436; 33, 376.

Chloride of Phosphorus; Gay-Lussac & Thénard. *Recherches*, 2, 176.—H. Davy, *Schw.* 3, 83 and 98; *Gilb.* 39, 6.—Berzelius, *Ann. Chim. Phys.* 2, 224.—Serullas, *Ann. Chim. Phys.* 42, 25; also *Schw.* 57, 366; also *Pogg.* 17, 161.

Oxy-chloride of Phosphorus; Wurtz, *N. Ann. Chim. Phys.* 20, 472; abstr. *Ann. Pharm.* 64, 245.

Chloride of Sulphur; Thomson, *Nichols. J. of Nat. Phil.* 6, 96; also *N. Gehl.* 6, 333. *Ann. Phil.* 15, 408; also *N. Tr.* 5, 2, 322.—H. Davy, *Elem. d. Chem. Theils d. Naturwissenschaft*, 253.—A. Berthollet, *Mém. d'Arcueil*, 1, 161; also *N. Gehl.* 6, 352.—Bucholz, *N. Gehl.* 9, 172.—Ridolfi, *Schw.* 22, 303.—Gaultier de Claubry, *Ann. Chim. Phys.* 7, 213.—Dumas, *Bullet. Philom. d. Sc.* 1825, 23.—*Ann. Chim. Phys.* 49, 204; also *Schw.* 65, 81.—H. Rose, *Pogg.* 21, 431; 24, 303; 27, 107; 42, 517 and 542.—Martens, *J. Chim. Med.* 13, 430. —Millon, *Compt. Rend.* 6, 207; also *J. pr. Chem.* 16, 57.—Marchand, *J. pr. Chem.* 22, 507.

Sulphate of Chloride of Sulphur; H. Rose, *Pogg.* 44, 291; 46, 167; 52, 69.—Regnault, *Ann. Chim. Phys.* 69, 170; 71, 445; also *J. pr. Chem.* 18, 93; 19, 243.

Chloride of Selenium; Berzelius, *Ann. Chim. Phys.* 9, 225.

Chloride of Iodine; Gay-Lussac, *Ann. Chim.* 91, 5; also *Gilb.* 49, 8.—Serullas, *Ann. Chim. Phys.* 22, 185; 38, 387; 43, 208; (also *J. Chim. Med.* 6, 336; *Pogg.* 18, 116; *N. Tr.* 21, 2, 256; 45, 59, 199, and 270; also *J. Chim. Med.* 7, 9 and 93; also *Pogg.* 21, 164; 46, 294. —Soubeiran, *J. Pharm.* 23, 49.—Kane, *Phil. Mag. J.* 10, 430; abstr. *J. pr. Chem.* 11, 250.

Metallic Chlorides and Hydrochlorates; Val. Rose. *Atomic proportions, A. Gehl.* 6, 22.—Gay-Lussac & Thénard, *Recherches*, 2, 94.—H. Davy, *Gilb.* 39, 43.—J. Davy, *Schw.* 10, 311.—A. Vogel. *Behaviour of Chlorides with Sulphuric acid, Schw.* 32, 51.

Chlorine, Halogen; Oxy-muriatic acid, Oxidated, Oxygenated, Dephlogisticated Muriatic Acid, Bleaching Acid; Chlore, Acide muriatique oxigéné; Chlorum, Acid muriaticum oxigenatum. In the gaseous state; *Chlorine gas, Chlorgas, Oxy-muriatic acid gas, Zündendes Salzgas, Gas acide muriatique oxigéné.*

History. From common salt, a substance known from the earliest times, the alchemists appear first to have obtained *Aqueous Muriatic Acid.* Priestley, with his mercurial pneumatic trough, discovered *Muriatic acid gas.* By treating manganese with muriatic acid, Scheele, in 1774, first obtained chlorine gas, which, in accordance with the existing doctrine of phlogiston, he regarded as *Dephlogisticated Muriatic Acid.* Berthollet, in 1785, showed, that in accordance with the antiphlogistic system of chemistry, just then rising into favour, this substance ought to be regarded as *Oxygenated Muriatic Acid;* and this view was adopted and maintained its ground till 1809. In that year, however, Gay-Lussac & Thénard, showed, by arguments founded on numerous experiments, that the chemical relations of chlorine might all be explained on the supposition of its

being an elementary substance. Sir H. Davy, in 1810, was the first to give the preference to this now almost universally adopted theory: he also gave to the substance in question its present name of CHLORINE.

The bleaching compounds obtained by bringing chlorine in contact with alkaline solutions were known as early as the time of Berthollet. They were long regarded as chlorides of the alkalis, till Berzelius suggested the idea that they might be mixtures of metallic chlorides with alkaline chlorites, the acid of which probably contained 3 atoms of oxygen to 1 of chlorine.

$$4KO + 4Cl = 3KCl + KO, ClO^3.$$

Balard, in 1834, showed that the bleaching compounds are mixtures of metallic chlorides with alkaline hypochlorites, and he obtained *Hypochlorous acid* in the free state. In 1815, Sir Humphry Davy and Count Stadion simultaneously discovered *Oxide of Chlorine* (also called *Chlorous acid*), which had previously been noticed by Chenevix, but mistaken for chloric acid. Berthollet first showed how to prepare some of the chlorates: these were more minutely examined by Chenevix in 1802; and in 1814 Gay-Lussac first succeeded in isolating *Chloric acid* from them. *Perchloric acid*, discovered in 1815 by Count Stadion, was afterwards more particularly examined by Serullas.

Chlorous acid (ClO^3) was discovered by Millon; also the *Chlorochloric* and *Chloro-perchloric acids* formed by the union of chlorous acid with chloric and perchloric acid respectively.

Phosgene gas was discovered by John Davy; *Chloride of Boron* by Berzelius, in 1824; *Terchloride of Phosphorus* by Gay-Lussac & Thénard, in 1808; *Pentachloride of Phosphorus* by Sir H. Davy; *Oxychloride of Phosphorus* by Wurtz; *Chloride of Sulphur* by Hagenmann, in 1781 (*Crell. N. Entd.* 4, 74); and by Thomson in 1804; a compound of oxygen, chlorine, sulphur, and carbon, by Berzelius & Marcet, in 1813; and several others (which, however, rather belong to the department of organic chemistry) by Kolbe; *Chloride of Selenium* by Berzelius; *Chloride of Iodine* by Gay-Lussac; *Chloride of Bromine* by Balard. The characteristic properties of the metallic chlorides were especially examined by Gay-Lussac & Thénard.

Sources. Chlorine occurs in considerable quantities in all three kingdoms of nature, sometimes as hydrochloric acid, sometimes as sal-ammoniac; also in the chlorides of potassium, sodium, calcium, magnesium, lead, mercury, and silver, and in certain ores of copper.

Preparation. 1. *In the gaseous state.* (*a.*) By heating manganese with strong hydrochloric acid. (*Sch.* 64 or 73.)

$$MnO^2 + 2HCl = MnCl + 2HO + Cl$$
$$\text{or: } MnO + 2HCl = MnO, HCl + HO + Cl.$$

About 4 parts of acid are required for 1 part of manganese. (*b.*) By heating manganese with common salt and dilute sulphuric acid. (*Sch.* 79.)

$$MnO^2 + NaCl + 2SO^3 = MnO, SO^3 + NaO, SO^3 + Cl.$$

The proportions required are: 1 At. manganese, 1 At. common salt, and 2 At. sulphuric acid; but it is better to use $\frac{1}{2}$ At. more sulphuric acid, as otherwise the decomposition is not complete till the mass becomes dry. (Hesse.) For 1 part of common salt, $\frac{3}{4}$ pt. of good manganese and 2 parts oil of vitriol diluted with 1 part water are required: if the manganese consists of hydrate of manganic oxide (Mn^2O^3, HO), the proportions

are: 1 part common salt, 1 manganese, and $2\frac{3}{4}$ oil of vitriol diluted with half its weight of water. According to Döbereiner (*Schw.* 63, 480), bisulphate of soda mixed with water does not liberate chlorine from a mixture of common salt and manganese till the mixture has become dry; and the chlorine thus evolved is mixed with a very large quantity of vapour of chloride of manganese. Hesse (*Ann. Pharm.* 3, 61) combats this statement; and the author's experiments also show that this mixture evolves abundance of chlorine long before it becomes dry. The more finely the manganese is pounded, the more completely is it decomposed before drying.

The gas obtained by either of the preceding methods may be contaminated with hydrochloric acid gas and vapour of chloride of manganese. To free it from these impurities, it may be washed by passing it through a bottle containing water (*App.* 43). It is collected over hot water, inasmuch as cold water absorbs it abundantly.

¶ For preparing chlorine on the large scale (as for the manufacture of bleaching-powder), a new process has lately been introduced by Mr. Dunlop, in which the use of oxide of manganese is superseded by nitric acid. 1 At. nitric acid yields 2 At. oxygen to the hydrochloric acid, whereby it is converted into nitrous acid, and causes the evolution of 2 At. chlorine.

$$NO^5 + 2HCl = NO^3 + 2HO + 2Cl.$$

The economy of the process consists in absorbing the nitrous acid vapour by sulphuric acid, and introducing the nitrous acid in this form into the *leaden chamber*. (*Graham's Chemistry, New Ed.* page 460.)

Another manufacturing process, which has been patented in this country, consists in burning the hydrogen of hydrochloric acid at the expense of the oxygen of the air, whereby a mixture of chlorine and nitrogen gases is obtained. The hydrochloric acid gas mixed with air is introduced into a chamber containing red-hot bricks, and the resulting gaseous mixture passed through water to remove undecomposed hydrochloric acid. The chlorine thus obtained serves for the manufacture of chloride of lime. (Oxland, *Berz. Jahresb.* 26, 136.) ¶

2. *In the liquid state.* *a.* Hydrate of chlorine is put into a strong glass tube, the tube sealed, and heated to 38° (100° F.). The hydrate fuses and divides itself into two strata; the upper of these, which occupies three-fourths of the whole, is water coloured by a small quantity of chlorine; the lower is liquid chlorine. If the tube is bent with two arms, the chlorine may be distilled from one to the other, and thus separated from the water. (H. Davy & Faraday.) Chlorine gas is passed into 20 grammes of water contained in a cylindrical vessel, and kept at a temperature between 0° and 1°, till the water is converted into a stiff paste. The whole is then thrown upon a filter, to remove the excess of water—the hydrate of chlorine pressed between bibulous paper, which is frequently changed—then removed from the filter by means of a wooden spatula, and divided upon a glass plate into strips: in this form, it is thrust into the tube, which is held for the purpose close to the edge of the glass plate. All these operations must be performed as quickly as possible, and at a temperature only a little below 0°; for at −4° the hydrate freezes fast to the filter. The sides of the glass tube should be half a line in thickness, its width $3\frac{1}{2}$ lines, and its length at the commencement of the operation 4 inches. Before the hydrate is introduced, the tube must be drawn out a little, about $2\frac{1}{2}$ inches from the sealed end. The hydrate of chlorine is firmly pressed in with a ramrod to the thick-

ness of $1\frac{1}{2}$ inch. The tube is then inserted through a cork nearly as far as the part which has been drawn out—introduced into a vessel filled with a freezing mixture, so that the mouth of the vessel may be closed by the cork—drawn out at the narrow part into a long neck—cut off at that part—the sides of the neck thickened in the flame of a lamp, without actually sealing it—the tube left to cool—then taken for a few seconds out of the freezing mixture—then immersed in a fresh mixture, and strongly sealed at the moment when the gas within it begins to contract. (Biewend, *J. pr. Chem.* 15, 440.)—*b.* Chlorine gas dried by oil of vitriol may also be liquefied by pressure and cooling. (H. Davy & Faraday.)—*c.* Fuming hydrochloric acid and peroxide of manganese are sealed up together in a bent tube. At ordinary temperatures, a yellow film of liquid forms between the manganese and the acid; and if the empty arm of the tube is cooled 10° lower, this liquid distils over into it. (Niemann, *Br. Arch.* 36, 18.)—*d.* The longer arm of a bent glass tube is three-fourths filled with an intimate mixture of previously fused bisulphate of potassa, dried common salt, and manganese; upon this is placed a layer $1\frac{1}{2}$ inch thick of pieces of chloride of calcium; the shorter and empty arm of the tube is sealed, and the longer arm inserted into a gun-barrel, which is heated by coals heaped around it, while the short arm is kept cool. Liquid chlorine distils over into the latter, and when the longer arm cools, is not absorbed by its contents. This process may be performed in summer. (Mohr, *Ann. Pharm.* 22, 162.)

Tubes containing liquid chlorine must, if they likewise contain water (as when process *a* is adopted), be kept in the dark; otherwise the water will be decomposed and oxygen gas evolved, which will burst the tube.

Properties. 1. *In the liquid state.* Transparent, of a dark greenish-yellow colour (pure yellow—*Niemann*); very fluid; specific gravity = 1·33; does not solidify at — 17·8° (0° F.) [nor at — 220° F. (Natterer)]; its refracting power is less than that of water. (H. Davy & Faraday.) Does not conduct electricity (Solly; Kemp); does not attack the platinum electrodes; bleaches dry litmus-paper. (Kemp.)

2. *In the gaseous form.* [Tension, specific gravity, and refracting power (I., 261, 279—95).] Liquid chlorine, when the vessel containing it is opened, is instantly converted into gas: a small portion, however, is retained for a while in the liquid state, in consequence of the intense cold, probably amounting to — 40°, produced by the sudden evaporation of the other part. (Faraday.) Pale yellow gas (the denser gas which rests immediately on the surface of liquid chlorine is orange-yellow, not greenish-yellow). When perfectly dry, it neither freezes nor liquefies at a temperature of —40°. (H. Davy.) Incombustible: a wax taper plunged into it continues to burn with a feeble light, and copious deposition of soot: if introduced into the gas with a glowing wick, it is rekindled. (Trevelyan, *Phil. Mag. J.* 3, 72.) A burning slip of wood continues to burn in the gas for a short time only, and with a very feeble flame. Chlorine gas in the moist state destroys vegetable colours, without previously reddening any of them—litmus, for example. Since the dry gas has no action on dry litmus-paper, it would appear that the liquid state—whether produced by compression or by water—is essential to this action. (Kemp.) Chlorine destroys organic odours and infectious matters (*antimiasmatic fumigation*); has a very pungent and suffocating odour. When inhaled, even in small quantity, it excites sneezing, coughing, oppression, and choking; and if frequently inhaled, spitting of blood and fainting.

Atomic weight of chlorine: 35·48, H = 1, or 442·66 O = 1 (the double atom, Berzelius); 36 (Marignac, *Compt. Rend.* 14, 570); 35·46, H = 1, or 443·28, O = 1 (Marignac, *Berz. Jahresb.* 25, 33); 35·49, H = 1, or 443·669 (Maumené, *N. Ann. Chim. Phys.* 18, 41). Laurent (*Compt. Rend.* 14, 456) concludes from his own analyses that the number given by Berzelius is the correct one.

Compounds of Chlorine.

Chlorine and Water.

A. Hydrate of Chlorine. When chlorine is brought in contact with water, at a temperature a little below 0°, the two bodies unite and form a solid mass. The compound is obtained in a state of purity by introducing into a vessel filled with chlorine gas a quantity of water not sufficient to convert the whole into hydrate, and exposing the vessel for some days to a temperature of 0°. Arborescent, crystalline, pale yellow, translucent mass, having a density of 1·2, according to Faraday, and sometimes crystallizing in needles and rhombic octohedrons. Sometimes dendritic, sometimes granular, sometimes in crystals, which appear to belong to the regular system. (Biewend.) May be sublimed from one part of the vessel to another. (Faraday.) Does not conduct electricity. (Solly.)

	Calculation.		Faraday.
Cl	35·4	28·23	27·7
10HO	90	71·77	72·3
Cl, 10HO	125·4	100·00	100·0

Remains unaltered in the sealed tube at + 15·5° (and even at + 20°, Biewend); is resolved at 38° into chlorine-water and free chlorine, which separates as a distinct liquid stratum. On subsequent cooling to 21°, (often not till cooled to 0°, and imperfectly when at rest, *Biewend*), the two strata combine, and reproduce the crystalline hydrate. (Faraday.) When exposed to the air, and gently warmed, the hydrate is resolved, with slight effervescence, into gaseous chlorine and chlorine-water. The hydrate acts on ammonia, ammoniacal salts, and alcohol, in the same manner as free chlorine. (Faraday.)

B. Aqueous Solution of Chlorine. *Chlorine-water, Liquid Oxymuriatic acid.* Water at ordinary temperatures absorbs about twice its volume of chlorine gas. (Dalton.) The solubility of chlorine in water increases from 0° to 9°, because, at this latter temperature, the chlorine is still in the state of hydrate; but from this point upwards the solubility continually diminishes, and at 100° is almost nothing. (Gay-Lussac. *Ann. Chim. Phys.* 70, 407.) Pure water at 15° absorbs rather more than twice its volume of chlorine gas; but water saturated with chloride of potassium takes up one-third less. Water saturated with chlorine at 6° (42·8° F.) has a specific gravity of 1·003. (Berzelius.) It is yellowish, has the odour of the gas, and tastes not acid, but bitter. Freezes at about 0°, and is then, according to Faraday, resolved into hydrate of chlorine, and ice which is free from chlorine. It is gradually decomposed, especially when exposed to light, into aqueous hydrochloric acid and oxygen

gas. Whether the chlorine dissolves in the water without alteration, or whether it is first converted, on the one hand, into hydrochloric acid by taking oxygen from the water, and, on the other, into hypochlorous acid by taking oxygen from the water, is a question which must for the present remain undecided. At all events, the liquid has the same odour, and exhibits in other respects the same characters as the gas itself.

CHLORINE AND OXYGEN.

The affinity of chlorine for oxygen is even feebler than that of iodine and bromine for the same element; the two bodies cannot be made to combine directly.

A. HYPOCHLOROUS ACID. ClO.

Acide Hyperchloreux, Unterchlorige Säure.

Formation. 1. Chlorine and mercuric oxide form protochloride of mercury (or oxychloride, if the oxide is in excess), and hypochlorous acid. (Balard; Gay-Lussac.)

$$HgO + 2Cl = HgCl + ClO.$$

If the oxide of mercury be digested in chlorine-water, $\frac{5}{6}$ of the liquid distilled off, and $\frac{1}{6}$ of water added to the distillate, the mixture so formed possesses the same degree of bleaching power as the original solution, although the quantity of chlorine contained in it is only half as great, one half of the bleaching power being in fact due to the oxygen. (Gay-Lussac.)—2. When chlorine is brought in contact at ordinary temperatures with aqueous solutions of the alkalis, and a few other of the stronger bases, or with the compounds of these bases with the weaker acids, as carbonic or acetic acid, the chlorine not being in excess, a metallic chloride and a salt of hypochlorous acid are produced.

¶ 3. By the action of chlorine on various salts. When chlorine is passed into a solution of terbasic phosphate of soda ($3NaO, cPO^5$) till it is no longer absorbed, a liquid is obtained, having strong bleaching properties, and yielding hypochlorous acid when distilled; the residue in the retort has a strong acid reaction, and appears to consist of a mixture of 1 At. phosphate of soda and 2 At. chloride of sodium. Similar results are obtained with the ordinary phosphate, and the bibasic pyrophosphate of soda, excepting that the latter gives up only one atom of base. The normal sulphates of soda, sesqui-oxide of iron, oxide of zinc, protoxide of manganese, and protoxide of copper, and the double sulphate of alumina and potassa, yield a distillate of hypochlorous acid, and a residue consisting of chloride and acid sulphate; even sulphate of lead is slightly decomposed. Nitrate and chromate of potassa also yield hypochlorous acid, when treated with chlorine. (Williamson, *Ann. Pharm.* 54, 142.)¶

Preparation. In the gaseous state. 1. Finely pounded mercuric oxide (or sulphate, *Gay-Lussac*,) diffused through 12 times its weight of water, is introduced into a bottle filled with chlorine gas—the bottle shaken till the chlorine is absorbed, which soon takes place—the solution of hypochlorous acid immediately filtered from the brown oxychloride of mercury, and purified by distillation in vacuo. The acid solution thus obtained is weak, but may be concentrated by repeated fractional distillation of the portion

which first passes over. The aqueous solution having been concentrated in this manner, as far as possible, the anhydrous gaseous acid may be obtained from it, by introducing the liquid into a receiver filled with, and standing over mercury, and adding by degrees—so as to avoid any rise of temperature, which would cause an explosion—about an equal volume of dry nitrate of lime, or glacial phosphoric acid (which latter must be free from ammonia, and consequently must not have been prepared from phosphate of ammonia). The gas is evolved with effervescence, and the solution of nitrate of lime, or phosphoric acid, which is produced, protects it from the decomposing action of the mercury. (Balard.) Gay-Lussac found that this method yielded but a very indifferent result, when nitrate of lime was used.—2. A bottle of the capacity of 100 – 150 cubic centimetres having been filled with perfectly dry chlorine gas, a glass tube closed at the bottom, two-thirds filled with dry mercuric oxide, and above that with dry fine sand, is introduced into it—the bottle closed with a glass stopper, the upper third of which is smeared with tallow, so that the mouth may be completely closed, but the gas may not act upon the tallow—and shaken, so that the sand and oxide may fall out of the tube, and the oxide may act on the gas. In a few minutes, the chlorine is decolorized, and converted into half its bulk of hypochlorous acid gas. If the stopper be removed under mercury, the mercury enters and fills one-half of the bottle; water absorbs the gas suddenly and almost completely. But the excess of mercuric oxide often exerts a decomposing action on the gas, and liberates oxygen from it. (Gay-Lussac.)

¶ According to Gay-Lussac, the mercuric oxide prepared in the wet way, *e. g.* by precipitation with caustic potash, is best adapted for this process, and the gas produced by its action upon chlorine is colourless. Pelouze, however, finds that the oxide thus prepared acts with such violence on chlorine as to cause a considerable rise of temperature, whereby the hypochlorous acid is decomposed, and the only products obtained are chloride of mercury and oxygen gas. But if the oxide of mercury, before being used, is strongly heated in a sand-bath (the temperature being of course kept below the decomposing point) it afterwards acts less forcibly and without causing rise of temperature, and yields chloride of mercury and hypochlorous acid gas: moreover, the gas thus obtained is not colourless, but has a yellow tint, inclining more to red than that of chlorine.—3. Hypochlorous acid gas may be obtained at once in the anhydrous state by passing dry chlorine gas over mercuric oxide contained in a glass tube surrounded with fragments of ice or immersed in cold water. Chloride of mercury is then formed, and hypochlorous acid disengaged in the form of a yellow gas, which may be collected over mercury. It cannot, however, be kept over mercury, as it is gradually decomposed by that liquid; it must therefore be collected in stoppered bottles, having the upper part of the stopper smeared with grease, each bottle being removed as soon as it is filled; or the gas may be collected by displacement in a series of bottles connected together, the portion which issues from the last being absorbed by water, so that none may be wasted. The oxide of mercury used in this process must be prepared by precipitation with caustic potash and dried at 300° (572° F.). The red oxide obtained by igniting the nitrate or by prolonged ebullition of mercury is not acted on by dry chlorine. (Pelouze, *N. Ann. Chim. Phys.* 7, 179.)

b. In the liquid state. Dry hypochlorous acid gas, obtained by Pelouze's method (3), is passed into a *U*-tube cooled to –20° (–4° F.). (Pelouze).

Properties of the liquid acid. Deep orange-coloured liquid, heavier than water. Does not boil or volatilize till heated to 21° (69·8° F.). Nevertheless, it is apt to explode with violence even while surrounded with a freezing mixture; hence great care is requisite in manipulating with it. Does not alter the metallic lustre of antimony. When thrown into water it first sinks to the bottom, and then dissolves, provided the water is in sufficient quantity. If not, a yellow saturated solution is formed above the part which remains undissolved. If the saturated solution be diluted with water, its colour becomes fainter, and ultimately disappears altogether. (Pelouze.) ¶

Of the Gas. Yellow, not much darker than chlorine (Balard); yellow, somewhat inclining to red (Pelouze); colourless (Gay-Lussac); *vid.* p. 295. Of very powerful odour, more resembling that of chlorine than that of chloric oxide, but different from both. (Balard.)

Calculation, according to Balard.				Vol.	Sp. gr.
Cl	35·4	81·6	Chlorine gas	1	2·4543
O	8·0	18·4	Oxygen gas	½	0·5546
ClO	43·4	100·0	Hypochlorous acid gas	1	3·0089

Decompositions. 1. One volume of the gas is resolved by heat, with explosion and development of light, into a mixture of 1 volume of chlorine gas and a half volume of oxygen. The temperature required to explode it is, at most, a little higher than that required to explode chloric oxide; but sometimes it explodes while being transferred from one vessel to another. (Balard.) According to Gay-Lussac, it detonates very easily, sometimes even at ordinary temperatures. When exposed to sunshine, it is decomposed in the course of a few minutes, in the same manner, but without detonation. In diffused daylight it remains unaltered for some hours.

2. When mixed with hydrogen it explodes violently on the approach of a burning body, and forms a white cloud of hydrated hydrochloric acid. Charcoal causes the gas to explode at ordinary temperatures, probably in consequence of the heat produced by absorption; the resulting gaseous mixture contains a small quantity of carbonic acid, besides chlorine and oxygen. Hypochlorous acid gas mixed with carbonic oxide is converted in a few hours into phosgene gas (and carbonic acid?). Aqueous hypochlorous acid is not decomposed either by charcoal or by carbonic oxide. Phosphorus decomposes the gas at ordinary temperatures, producing flame and explosion, and forming phosphoric acid and chloride of phosphorus with a little free chlorine; with the aqueous acid, it forms phosphoric acid and a small quantity of hydrochloric acid, with evolution of chlorine. Hypophosphorous and phosphorous acids are likewise converted into phosphoric acid by contact with solution of hypochlorous acid, heat being evolved and chlorine gas set free. Phosphuretted hydrogen explodes with this gas at ordinary temperatures: the residual gas contains chlorine with a small quantity of oxygen. With the aqueous acid, phosphuretted hydrogen produces phosphoric and hydrochloric acid, with evolution of chlorine. The gas explodes by contact with sulphur at ordinary temperatures, emitting a brilliant light, and forming sulphurous acid and chloride of sulphur, whilst part of the chlorine is set free. When sulphur is digested in the aqueous solution of the acid, chlorine is evolved, and sulphuric acid, together with a small quantity of chloride of sulphur, produced. A mixture of hypochlorous and sulphurous acid gases condenses in a few hours, with formation of sulphuric acid (while the chlorine com-

bines with the mercury over which the gaseous mixture is placed). Sulphurous acid gas passed through the aqueous solution produces sulphuric acid and liberates chlorine. Hydrosulphuric acid gas produces a pale blue flame with gaseous hypochlorous acid: when passed, not in excess, through the aqueous solution, it produces sulphuric acid and water, with rise of temperature and evolution of chlorine gas. Bisulphide of carbon introduced into the gas at ordinary temperatures produces slight detonation, and forms carbonic acid, sulphurous acid, and chloride of sulphur, while chlorine is set free: with the hydrated acid it forms carbonic, sulphuric, and hydrochloric acid. Sulphide of phosphorus introduced into the aqueous solution of the acid produces sulphuric, phosphoric, and hydrochloric acid, with evolution of chlorine gas, gentle at first, but increasing in rapidity as the temperature rises. Selenium at ordinary temperatures causes the gas to explode slightly: in the solution, it is converted into selenic acid, with evolution of chlorine. Selenious acid is likewise converted into selenic acid by the action of hydrated hypochlorous acid. Iodine absorbs the gas, producing iodic acid and chloride of iodine: when put into the solution, it causes rise of temperature and evolution of chlorine, and is converted into iodic acid, together with a small quantity of chloride of iodine. Hydriodic acid gas mixed with gaseous hypochlorous acid causes rise of temperature and decomposition: hydriodic acid gas or its aqueous solution mixed with aqueous hypochlorous acid produces iodic acid, with rise of temperature and evolution of chlorine. Bromine absorbs the gas, producing bromic acid and chloride of bromine: from the solution it liberates chlorine, and is converted into bromic acid. Hydrobromic acid water mixed with excess of the hydrated acid produces bromic acid, chloride of bromine, hydrochloric acid, and chlorine.

3. Hypochlorous acid gas mixed with hydrochloric acid gas yields water and chlorine: it has no action on nitrous oxide: it explodes with ammoniacal gas, and the aqueous solution mixed with aqueous ammonia produces water and chloride of nitrogen, or water, nitrogen, and chlorine.

4. Potassium burns on the surface of the aqueous acid without evolving chlorine, and produces chloride of potassium and hypochlorite of potassa.

$$2K + 2ClO = KCl + KO, ClO.$$

Arsenic causes the gas to explode with a vivid light, producing arsenic acid and a small quantity of chloride of arsenic, and liberating chlorine gas. Many metals wrapped up in sized paper absorb the gas rapidly, forming an oxide and a chloride, till the heat evolved by the action causes the gas to explode. Silver-leaf merely forms chloride of silver, and liberates oxygen, till the heat evolved gives rise to explosion. Mercury absorbs the whole of the gas, with the exception of a small quantity of oxygen, and forms red oxychloride of mercury. Phosphide of calcium causes the gas to explode violently, with separation of chlorine: the sulphides of barium, antimony, tin, and mercury produce explosion in a few seconds, with formation of chloride of sulphur. The aqueous acid converts arsenic into arsenic acid and a small quantity of chloride of arsenic, with evolution of chlorine gas; dissolves iron, converting it into sesqui-chloride, and evolving chlorine gas [oxygen ?]; dissolves copper, converting it into protochloride, with evolution of chlorine and a small quantity [?] of oxygen; converts mercury, when shaken up with it, almost instantly into oxy-chloride; silver-filings into chloride of silver, with rapid evolution of oxygen gas; does not act, when dilute, upon antimony, bismuth, zinc, tin, or lead, excepting in presence of an acid which can form a soluble salt

with the oxide of the metal, in which case the hypochlorous acid causes rapid oxidation of the metal and evolution of chlorine. Concentrated hypochlorous acid acts gradually on the five metals just mentioned, because chloric acid is produced in it, and this supplies the place of sulphuric or nitric acid. Gold and platinum are not attacked by aqueous hypochlorous acid, even when mixed with sulphuric or nitric acid. The aqueous acid converts oxide of chromium into chromic acid, arsenious acid into arsenic acid, and the protoxides of manganese, tin, lead, cobalt and nickel, into the corresponding oxides of the highest degree of oxidation, the action being in all cases attended with liberation of chlorine: oxide of silver, on the other hand, is converted into chloride, with evolution of oxygen gas and a small quantity of chlorine. With metallic sulphides, the aqueous acid forms sulphates, and sometimes also chloride of sulphur, with rise of temperature and evolution of chlorine. With the chlorides of the alkali-metals it forms alkaline hyperchlorites, with which a small quantity of chloride remains mixed; the chlorides of manganese, tin, lead, iron, cobalt, and nickel are converted by it into the corresponding highest oxides, with evolution of chlorine; and chloride of copper, into oxychloride.

5. Hypochlorous acid decomposes olefiant gas, oxalic acid, cyanogen, hydrocyanic acid, paper, litmus, indigo, and many other organic compounds. White unsized paper causes the gas to explode.

Combinations. a. With Water: *Aqueous Hypochlorous Acid.* Water absorbs the gas very quickly, probably taking up more than 100 times its volume. A portion of chlorine and oxygen gases always remains behind, because, in the preparation of the gas from the aqueous acid, partial decomposition takes place. (Balard.) *Preparation* (p. 294).

The aqueous acid may also be prepared by treating common chloride of lime with very dilute hydrochloric acid and distilling: the acid must be added in successive portions, with constant agitation, and in such quantity as to saturate less than half the lime. (Gay-Lussac.) ¶ Or chlorine gas may be passed into water in which finely divided chalk is suspended, whereupon chloride of calcium is formed and dissolves, and hypochlorous acid is set free: the acid may then be separated by rapid distillation. (Williamson.) ¶ The concentrated acid is yellowish: it has the odour of the gas, and a strong but not acid taste. A single drop of it placed upon the skin produces a brown stain, and destroys the epidermis in the course of half a minute: it corrodes more deeply than nitric acid.

When the solution is exposed to the air, the greater part of the acid volatilizes. At 100°, only a small portion escapes in the gaseous form; a much larger quantity on the addition of nitrate of lime or glacial phosphoric acid: oil of vitriol, on the contrary, separates a mixture of chloric oxide, chlorine, and a small quantity of oxygen gas. The aqueous acid is slowly decomposed in the dark, more quickly, however, in proportion as it is warmer and more concentrated. The concentrated acid, even when surrounded with ice, does not remain unaltered for more than a few days: a dilute solution resists decomposition for a longer time. The decomposition produced by the application of heat is not immediate; hence distillation is possible. When decomposition takes place, bubbles of chlorine gas rise through the liquid, and by agitation or addition of pulverulent substances, brisk effervescence takes place: the residual solution consists of chloric acid. (Balard.)

$$5ClO = Cl^5 + 4Cl.$$

The acid when heated for some time to 100°, evolves about 5 volumes of chlorine and 1 volume of oxygen, and leaves chloric acid. (Gay-Lussac.) On distilling an aqueous acid, which has a bleaching power of 909°—changing the receiver 9 times, so as to obtain 9 distillates, each containing $\frac{1}{10}$ of the liquid, and leave the remaining $\frac{1}{10}$ in the retort—the first distillate is found to have a bleaching power equal to 2500°, the second 1925°, the third 1470°, the fourth 943°, the fifth 624°, the sixth 400°, the seventh 222°, the eighth 106°, the ninth 80°, and the residue in the retort 0°. The sum of these degrees divided by 10 gives 822°; consequently, the acid loses only 87° of bleaching power by the incipient decomposition which takes place during distillation. It appears as if the decomposition took place only where the liquid is in contact with the sides of the vessel, while the inner portions sustain the boiling heat without decomposition, and volatilize unchanged within the gas-bubbles, consisting of chlorine and a little oxygen, which are generated at the sides of the vessel. When an acid of 1200°—1500° bleaching power is distilled, the decomposition is much more considerable: with an acid of 600°—700° bleaching power, on the contrary, it is very small, and from such an acid, if kept for some time at 100°, any free chlorine possibly present may be almost wholly expelled. (Gay-Lussac.) Light, especially solar light, greatly accelerates the decomposition. In direct sunshine, it takes place in a few seconds. In this decomposition, chlorine is likewise evolved, and the residue contains chloric, and sometimes also chlorous acid. (Balard.) A portion of oxygen is sometimes evolved together with the chlorine, and a small quantity of hydrochloric acid is also formed, together with the chloric acid, probably a secondary product resulting from the action of the chlorine on the water. (Gay-Lussac.) In the circuit of the voltaic battery, the aqueous acid gives no gas at the negative pole, but oxygen at the positive pole, pure at first, but afterwards mixed with chlorine. (For the other modes of decomposition of the aqueous acid, *vid.* pp. 297, 298.)

b. With Salifiable Bases: *Hypochlorites.* The aqueous acid decomposes the alkaline carbonates with effervescence. *Preparation.* 1. By bringing aqueous hypochlorous acid in contact with alkalis, magnesia, hydrated oxide of zinc or hydrated oxide of copper, rise of temperature being carefully avoided, and the acid not added in excess. No other salts of hydrochlorous acid are known. Since the combination is attended with evolution of heat, whereby the hypochlorite would be resolved into chloride and chlorate, the acid must be added to the alkaline solution by small portions at a time, stirring frequently, and keeping the liquid cool by immersing the containing vessel in cold water: moreover, the acid must not be added in excess, because then the same decomposition would take place. From hypochlorite of lime or baryta obtained in this manner, the hypochlorites of the soluble alkalis and of magnesia may be prepared by precipitation with a carbonate or a sulphate. The solution may be evaporated to dryness in vacuo at ordinary temperatures without decomposition, provided it contains an excess of alkali. (Balard.)—2. Hypochlorites are obtained mixed with chlorides—forming the so-called *Chlorides of the Alkalis*—when chlorine gas (in the proportion of somewhat less than 1 equivalent) is brought in contact with caustic fixed alkalis (magnesia included) or their carbonates, dissolved in or diffused through water, the temperature being kept as low as possible.

$$2KO + 2Cl = KCl + KO,ClO.$$

If the temperature should rise too high in consequence of the absorption,

oxygen gas will be evolved, and the hypochlorite partly resolved into chloride and chlorate. Excess of chlorine likewise brings about the decomposition of the hypochlorite into chloride and chlorate, with evolution of a quantity of oxygen gas, amounting to between 2 and 3 per cent. of that contained in the hypochlorous acid. This decomposition takes place even when the liquid is so dilute that no chlorate crystallizes out; it likewise takes place with lime and magnesia. Hence only 6 atoms of chlorine should be added to 7 of alkali: in that case, 3 atoms of chloride are produced, and there remain 3 atoms of hypochlorous acid with 4 atoms of alkali. (Gay-Lussac.)

Chloride of lime having been obtained in this manner, the corresponding compounds of ammonia, potash, or soda may be obtained by precipitating its solution with the carbonates of these alkalis. When chlorine gas is passed through an aqueous solution of carbonate of potash previously saturated with chloride of potassium, a precipitate of chloride of potassium is produced—a proof that a fresh portion of that salt is formed by the action of the chlorine, and consequently that the chlorine does not combine directly with the alkali (Berzelius): a similar result is obtained with solution of carbonate of soda saturated with common salt. (Soubeiran.) When chloride of soda (obtained by decomposing chloride of lime with carbonate of soda) is evaporated to dryness in vacuo—by which it loses but very little of its bleaching power—and the residue digested in saturated solution of common salt, that liquid dissolves the hypochlorite of soda, and leaves a quantity of common salt amounting to 83 per cent. of the original residue. If the evaporation has not been carried quite to dryness, the cubes of common salt are covered with a mother-liquor, together with effloresced crystals of hypochlorite of soda. (Soubeiran.) When a mixture of chlorine and oxygen gases (about 2 vols. chlorine to 1 vol. oxygen) is passed through an aqueous solution of an alkali—potash, for example—the oxygen is absorbed, and a pure alkaline hypochlorite is obtained, not mixed with chloride, and consequently of double bleaching power. Common air may be used instead of oxygen. (Mackenzie, *Compt. Rend.* 6, 865; also *J. pr. Chem.* 16, 47.) Marchand (*J. pr. Chem.* 16, 48) corroborates this statement with reference to lime also. On the other hand, Otto (*N. Br. Arch.* 19, 160) found that the statement in question is incorrect, as far as potash is concerned: the author likewise observed not the slightest absorption of oxygen contained in a bottle, together with solution of carbonate of soda into which chlorine gas was passed. When chlorine is passed into aqueous solution of acetate of potash, a large quantity of it is absorbed, with corresponding disengagement of acetic acid. The product is a strongly bleaching yellow liquid, which evolves chlorine when treated with a stronger acid; gives off undecomposed acetic acid together with a small quantity of chlorine, when distilled, while chloride of potassium, chlorate and acid acetate of potash remain behind: when exposed to the air, it gradually gives up its chlorine and loses its bleaching power. (Liebig.) Raab (*Repert.* 32, 224) regards the chlorides of the alkalis as mixtures of metallic chlorides with peroxides of the metals and hydrate of chlorine. Millon (*J. Pharm.* 25, 595; also *J. pr. Chem.* 18, 291) regards them as peroxides in which part of the oxygen is replaced by chlorine. According to this view, since peroxide of potassium is KO^3, chloride of potash must be $KOCl^2$; and, since peroxide of sodium is NaO^2, chloride of soda must be NaOCl.

The hypochlorites have a caustic and astringent taste, thicken the saliva, produce small white spots upon the skin, and emit a peculiar sickly

odour when they come in contact with organic substances. They contain 1 atom of base combined with 1 atom of acid. (Gay-Lussac.) 1 At. KO dissolved in water and mixed with 2 At. ClO loses 1 At. ClO, when placed in vacuo over hydrate of potash at ordinary temperatures: the residue is a mixture of chloride of potassium and chlorate of potash. (Gay-Lussac.)

The aqueous solutions of the hypochlorites very slowly evolve oxygen gas when kept in the dark at ordinary temperatures. Such is the case with chloride of potash and chloride of lime, at least according to Berthollet and Marin. Mackenzie, on the other hand, maintains that the alkaline hypochlorites, at ordinary temperatures, and even near upon 100°, absorb oxygen and are converted into chlorates!

In diffused daylight, and more quickly in direct sunshine or by the aid of heat, the alkaline hypochlorites are resolved—generally with evolution of oxygen gas—into a metallic chloride and a chlorate, the decomposition taking place with greater facility as the alkali is less predominant. Mere evaporation in vacuo induces this decomposition, if the alkali is not in great excess. (Balard.) When hypochlorite of potash containing 1 atom of base to 1 atom of acid is kept for some time at 100°, it evolves 13 per cent. of the oxygen contained in the acid; but if there be 4 atoms of base to 1 atom of acid, the oxygen evolved amounts to 36 per cent.: with a few exceptions, the quantity of oxygen evolved is greater, the more the alkali is in excess. Powdered manganese added to the solution increases the quantity of oxygen evolved, and at the same time communicates a red colour to the liquid, from formation of permanganic acid. The residue in all cases contains chloride of potassium and chlorate of potash. Chloride of potash behaves in the same manner as the pure hypochlorite. (Gay-Lussac.) Aqueous chloride of potash evolves a portion of its oxygen when concentrated by boiling, and on passing to the solid state gives off a small quantity of chlorine: the solution and evaporation must however be repeated several times before the bleaching compound is completely converted into chloride of potassium and chlorate of potash. Aqueous solution of chloride of potash evolves a small quantity of chlorine when evaporated in vacuo. Solution of chloride of lime also, when concentrated by boiling, deposits lime, and evolves, first oxygen, and lastly, on passing to the dry state, chlorine; chlorate of lime is also formed. (Soubeiran.) Chlorides of the alkalis containing excess of alkali may be evaporated to dryness even at 50° (122° F.), without being resolved into chlorate and metallic chloride, and the residue still retains considerable bleaching power. (Martens.)

The hypochlorites are decomposed at ordinary temperatures, with loss of bleaching power, by excess of hypochlorous acid, the products being a chlorate and a metallic chloride. (Balard.) This decomposition is produced with even greater facility by the addition of free chlorine to the hypochlorite: part of the metallic oxide is then converted into chloride—while the hypochlorous acid is liberated, and, at the same time, a fresh quantity of it is formed by the combination of part of the chlorine with the oxygen of the metallic oxide. (Gay-Lussac.) Part of the salt is probably decomposed in this manner:

$$KO, ClO + 2Cl = KCl + 2ClO;$$

and the excess of hypochlorous acid thus produced acts on the rest of the salt as above described. The chlorides of the alkalis are also completely converted by excess of chlorine or hypochlorous acid, with the aid of heat, into chlorate and metallic chloride, with evolution of chlorine and a

small quantity of oxygen. (Gay-Lussac.) Aqueous solutions of the alkalis saturated with chlorine yield hypochlorous acid by distillation, the residue containing metallic chloride with a trace of chlorate. If hydrated oxide of zinc or copper be saturated with chlorine and the liquid heated, a distillate of hypochlorous acid is likewise obtained. (Martens; *vid.* also Williamson, *Ann. Pharm.* 54, 133.)

The aqueous solutions of the hypochlorites exert the same kind of oxidizing action as the solution of the acid itself, being themselves at the same time converted into chlorides. They convert phosphorus or phosphorous acid into phosphoric acid; sulphur or sulphurous acid into sulphuric acid; iodine into iodic acid; nitric oxide, absorbing it rapidly, into nitric acid; arsenic, which is brightened by the action, into arsenic acid; iron rapidly into ferric oxide; tin and copper, with evolution of a portion of chlorine and oxygen, into oxychlorides; and mercury likewise into oxychloride: they also convert most metallic oxides of a lower degree into oxides of the highest degree of oxidation, and freshly precipitated metallic sulphides into sulphates. On the other hand, they slowly convert silver into chloride, with evolution of oxygen. On gold and platinum they have no action. (Balard.) The chlorides of the alkalis in the state of aqueous solution act in the same manner. They convert phosphorus, sulphur, iodine, and arsenic into acid,—without evolution of chlorine, if the combustible body is in excess, with evolution of chlorine if it is not—because, in the latter case, the acid formed by the oxygen derived from the hypochlorous acid combines with the base and sets the chlorine free. They convert iron almost instantly into a red powder consisting of ferric oxide free from chlorine; mercury into a grey pulverulent oxide free from chlorine; and metallic sulphides, such as sulphide of lead or dissolved sulphide of barium, into sulphates. Antimony, zinc, tin, and copper, immersed in solution of chloride of lime, are converted into oxychlorides, the tin causing a slow, the copper a quicker evolution of oxygen gas. Finely divided silver immersed in chloride of lime is slowly converted into chloride of silver with a mere trace of oxide, while lime is set free. (Soubeiran.)

The behaviour of hypochlorites with heavy metallic oxides has only been examined with the chlorides of the alkalis. Chloride of lime gives with sulphate of manganous oxide a brown-black precipitate of hydrated peroxide of manganese. (Phillips.) Chloride of lime in excess gives with nitrate of lead a white precipitate of chloride of lead, which however soon turns yellow, and afterwards brown; because the liquid, which contains hypochlorite of lime, converts the chloride of lead into peroxide, with evolution of chlorine. In the first instance, $CaCl + CaO, ClO$ with PbO, NO^5 forms $PbCl + CaO, NO^5 + CaO, ClO$; subsequently, CaO, ClO and $PbCl$ form $PbO^2 + CaCl + Cl$. (Balard.) If the nitrate of lead is in excess, the white precipitate first produced is turned brown in the same manner by the hypochlorite of lead contained in the solution; and the liquid when filtered from the precipitate becomes turbid, and deposits peroxide of lead, with evolution of chlorine. (Berzelius.)

$$PbO, ClO = PbO^2 + Cl.$$

From nitrate of mercurous oxide chloride of lime precipitates calomel, which quickly changes to red oxychloride; whereupon, the supernatant liquid loses its originally strong bleaching power, and becomes rich in corrosive sublimate. (Balard.) Chloride of lime so far neutralized with nitric acid that it no longer smells of chlorine, gives with nitrate of silver a

white precipitate of chloride of silver. The liquid filtered from this precipitate soon loses its strong bleaching power and acquires an acid reaction, while chloride of silver is precipitated and chlorate of silver remains in solution. (Berzelius, Balard.) Chloride of lime not neutralized by nitric acid gives with small quantities of nitrate of silver a black precipitate of peroxide of silver; the supernatant liquid mixed with a larger quantity of the silver-salt suddenly evolves oxygen gas, with violent effervescence, and loses its bleaching power. (Berzelius.) The black precipitate is a mixture of chloride and oxide of silver; the liquid, as it passes through the filter, effervesces violently and loses its bleaching power. Chloride of lime converts oxide of silver into chloride, with violent evolution of oxygen, derived partly from the oxide of silver, partly from the hypochlorous acid. (Balard.)

The hypochlorites destroy organic colouring matters: in other words, they bleach. If the salt contains excess of alkali, no bleaching takes place till an acid is added. If to 1 atom of potash dissolved in water and turned blue by litmus, hypochlorous acid be added in successive small portions, no decolorization takes place till about 0·9 At. acid has been added; but if the potash is in combination with carbonic acid, the first drops of hypochlorous acid produce decolorization. (Gay-Lussac.) Carbonate of potash mixed with a small quantity of chlorine bleaches litmus; caustic potash or lime similarly treated does not—except on the addition of an acid; *e. g.* on passing carbonic acid gas through the liquid. (Gm.) A given quantity of chlorine will bleach the same quantity of solution of sulphate of indigo, whether it be combined with water or with an alkaline carbonate (Welter; Soubeiran); but of colouring matters which do not contain a free acid—tincture of litmus, for example, the latter compound bleaches about $\frac{2}{3}$ less than the aqueous solution, and subsequent addition of acid to the mixture produces no further decolorization; whereas, if the acid be added to the chloride of the alkali or to the colouring matter, before the two are mixed, the bleaching action is as strong as that produced by chlorine-water. (Soubeiran.) Bibulous paper becomes rotten by contact with salts of hypochlorous acid, the action being accompanied by rise of temperature, which gives rise to evolution of oxygen gas and a small quantity of carbonic acid, and to the formation of chlorate and metallic chloride: if the action takes place with considerable quantities of material, the paper sometimes becomes so hot that it takes fire. (Balard.)

Nearly all acids decompose the hypochlorites, combining with the base and expelling the acid; this effect is produced even by a stream of carbonic acid (reciprocal affinity*). A hypochlorite evaporated to dryness and then treated with concentrated phosphoric acid yields hypochlorous acid gas, mixed however with a small quantity of free chlorine, because a portion of metallic chloride is formed during the evaporation. (Balard.) Hypochlorites dissolved in water are but partially decomposed by carbonic acid, because the hypochlorous acid remains dissolved in the liquid: if this be distilled off, a fresh addition of carbonic acid will liberate another portion, and so on. (Gay-Lussac.) The chlorides of the alkalis mixed

* According to Williamson (*Ann. Pharm.* 54, 133), hypochlorous acid has not, under any circumstances, the power of expelling carbonic acid from its combinations, unless it is itself decomposed at the same time: so that, when chlorine is passed into the solution of an alkaline carbonate, the hypochlorous acid produced does not combine with the base, but remains free, and may be obtained by distillation. On this is founded the mode of preparing the aqueous acid described on page 298. From this it would appear that the reciprocity of affinities above alluded to does not really exist. [W.]

with excess of sulphuric acid, or any other of the stronger acids, evolve nothing but chlorine, because the oxygen of the hypochlorous acid is expended in oxidizing the metal of the chloride:

$$KCl + KO,ClO + 2SO^3 = 2(KO,SO^3) + 2Cl.$$

But if sulphuric or nitric acid diluted with 20 parts of water be poured in a very fine stream, with constant agitation, into solution of chloride of potash or chloride of lime, and in such quantity as barely to saturate the alkali combined with the hypochlorous acid, the metallic chloride also present in the solution remains undecomposed, and hypochlorous acid is obtained on distilling the liquid. A chloride of an alkali likewise yields hypochlorous acid by distillation after chlorine has been added to it. (Gay-Lussac).

Euchlorine. Protoxide of Chlorine.

A gas discovered by Sir Humphry Davy, which, like hypochlorous acid, contains 1 atom of chlorine to 1 atom of oxygen, but must be regarded, not as a true chemical compound but as a mixture of chloric oxide gas and free chlorine. It is evolved on carefully heating 1 part of chlorate of potassa with 2 parts of hydrochloric acid, and 2 of water (or even with stronger hydrochloric acid, Soubeiran), and may be purified from free chlorine by agitation with mercury. (H. Davy.)—This mode of purification cannot be adopted; for the gas is gradually but completely absorbed by mercury. (Soubeiran.)

This gas is of a brighter yellow than chlorine, bleaches litmus, smells strongly of chlorine, and at the same time like burnt sugar.

Euchlorine explodes when heated (the heat of the hand being sometimes sufficient to produce violent explosion)—emitting a vivid light, and often fracturing the containing vessel: it is well, therefore, when preparing it, to protect the face by a mask. In this manner, 1 volume of euchlorine is resolved into 1 volume of chlorine and half a volume of oxygen. The behaviour of euchlorine with combustible bodies is, for the most part, the same as that of chloric oxide (*q. v.*).

The discoverer of euchlorine himself afterwards admitted the correctness of regarding this gas as a mixture of 3 measures of chlorine gas and 2 measures of chloric oxide. For he found that, when euchlorine is treated with water, a quantity of chlorine always remains unabsorbed, and the solution exhibits the same properties as water saturated with chloric oxide. This result is still more clearly established by the experiments of Soubeiran, from which it appears that when water is saturated with euchlorine (in which case chlorine always remains behind) and the absorbed gas driven out by warming the liquid; this gas is resolved by heat into about equal volumes of chlorine and oxygen.* Hence the gas absorbed by the water contains only half as much chlorine as the original gas. When water saturated with euchlorine is agitated with calomel (Hg^2Cl), the calomel absorbs the whole of the free chlorine, forming corrosive sublimate ($HgCl$); and the gas subsequently evolved by the application of heat exhibits the characters of chloric oxide, yielding when exploded, 1 vol. chlorine to 2 vols. oxygen. Hence

* Consequently, 1 At. chlorine to 2 At. oxygen. This compound, ClO^2, is usually considered to be wanting in the series of oxygen-compounds of chlorine: Berzelius, however, regards the experiment of Soubeiran above described, as a proof, not only of its existence as a distinct compound, but of its isolation having been actually effected. (Traité de Chimie, I., 558.) [W.]

pure chloric oxide is obtained when the gas evolved from chlorate of potassa by the action of hydrochloric acid is passed through water surrounded with ice and having calomel diffused through it. (Soubeiran.)

The idea that euchlorine is a definite chemical compound rests only on the fact of its being always constituted in the same proportions, and always being resolved by explosion into 2 volumes of chlorine and 1 of oxygen. Hence, when chlorate of potash is heated with hydrochloric acid, the gaseous mixture evolved must always consist of 3 measures of chlorine gas and 2 of chloric oxide. This may perhaps be explained as follows:—

$$4(KO, ClO^5) + 12HCl = 4KCl + 12HO + 3ClO^4 + 9Cl.$$

According to this formula, 9 atoms of chlorine are evolved for 3 atoms of chloric oxide, or 3:1; and since chlorine is a mon-atomic gas and chloric oxide is di-atomic (I., 53, 66, 67), this proportion gives 3 volumes of chlorine to 2 volumes of chloric oxide. (*Vid.* H. Davy, *Schw.* 3, 256.—*Ann. Chim. Phys.* 1, 76.—Gay-Lussac, *Ann. Chim. Phys.* 8, 410.—Soubeiran, *Ann. Chim. Phys.* 48, 113.—J. Davy, *N. Ed. Phil. J.* 17, 49.)

Millon regards euchlorine as a mixture of free chlorine with chlorochloric acid. (*Vid.* p. 314.)

¶ B. Chlorous Acid. ClO^3.

Acide Chloreux, Chlorige Säure.

Formation.—1. By the deoxidation of chloric acid. When a mixture of nitric acid and chlorate of potash is treated with various deoxidizing agents at a temperature below 57° (135° F.), the chloric acid is deprived of 2 atoms of oxygen and reduced to the state of chlorous acid, which escapes in the form of gas. The decomposition of the chloric acid appears to be effected through the medium of nitrous acid, which is formed from the nitric acid by the action of the deoxidizing agent.

$$NO^3 + ClO^5 = NO^5 + ClO^3.$$

a. Perfectly pure nitric acid of specific gravity 1·405 dissolves chlorate of potash without evolution of gas, and forms a colourless solution, provided the temperature be kept below 57°; but if the nitric acid contains nitrous acid, the addition of the chlorate of potash immediately produces a yellow colour, arising from the formation of chlorous acid. The same effect is produced if the chlorate of potash contains chloride of potassium, or if the nitric acid is contaminated with hydrochloric acid, because in either of these cases nitrous acid is formed. *b.* When a stream of nitric oxide gas is passed into a solution of chlorate of potash in nitric acid, at a temperature of 40° — 45° (104° — 113° F.), the nitric acid converts the nitric oxide into nitrous acid ($2NO^2 + NO^5 = 3NO^3$), and this compound converts the chloric acid into chlorous acid. Nitric oxide alone has no action either on chlorate of potash or on free chloric acid.—*c.* Most metals act upon a mixture of nitric acid and chlorate of potash in such a manner as to form chlorous acid: the metal is oxidized at the expense of a portion of the nitric acid, and nitric oxide is produced—and this gives rise to the action already described in *b.* Zinc produces but a feeble action in a mixture of nitric acid and chlorate of potash at 18° 64·4° F.); but at 24° (75·2° F.) the action is stronger, and chlorous acid is rapidly evolved. The vesel must be immersed in cold water to prevent the temperature from rising too high. If the nitric acid be so dilute that

the zinc, if acting on it alone, would liberate nitrous oxide instead of nitric oxide, no chlorous acid is evolved, but only nitrous oxide. Iron behaves like zinc, excepting that it requires a temperature of 40° (104° F.) to make it act; it must be used in rather thick pieces. Lead is not attacked till the liquid is raised nearly to the temperature at which chlorous acid is decomposed; hence an irregular, percussive action takes place, and free chlorine and oxygen pass off, mixed with undecomposed chlorous acid. Tin dissolves completely without evolution of gas, if the temperature be kept low: this results from the secondary action of the chlorous acid on the metal. On raising the temperature to 40° — 45°, a considerable quantity of chlorous acid is evolved. Mercury remains unaltered in nitric acid, either concentrated or dilute, to which chlorate of potash is added: the most violent action between the acid and the metal is instantly stopped by the addition of this salt. Similarly, with copper, silver, and bismuth. Antimony oxidizes very slowly in nitric acid to which chlorate of potash is added. This peculiar check to the oxidating action of nitric acid appears to be connected with the reconversion of nitrous acid into nitric acid by the action of the chloric acid.—*d.* Many oxides and acids of the lower degrees of oxidation act in the same manner as the metals: arsenious acid, for example, added to a solution of chlorate of potash in nitric acid causes an abundant evolution of chlorous acid.—*e.* Many organic substances, as sugar, gum, starch, dextrin, fibrin, albumen, wood, charcoal, muscular flesh, animal membrane, fat, oily acids, urea, citric acid, tartaric acid, volatile oils, and resins, also evolve chlorous acid from a mixture of nitric acid and chlorate of potash. In all these cases, it might be supposed that the decomposition of the chloric acid is produced by the direct action of the deoxidizing body—a metal, for example—the nitric acid merely serving to liberate the chloric acid from its combination with the alkali. But if that were the case, the same substances ought to evolve chlorous acid from an aqueous solution of chloric acid—which they do not; neither is chlorous acid evolved when sulphuric or hydrochloric acid is substituted for the nitric acid. The reduction of nitric acid to nitrous acid and its reoxidation by chloric acid appears to be essential to the process.

2. By the decomposition of hypochloric acid. (*Vid.* p. 296.)

Preparation.—1. A flask of the capacity of 300—400 cubic centimetres (about 20 cubic inches) is filled almost to the neck with a mixture of 1 part tartaric acid, 2 of chlorate of potash, 6 of ordinary nitric of sp. gr. 1·327, and 8 of water. The tartaric acid and chlorate of potash are first introduced, having been previously mixed but not pounded, and then the mixture of the acid and water. The action begins spontaneously after a few minutes at a temperature of 25° (77° F.); it may, however, be accelerated without risk of explosion by the application of a very gentle heat, as by placing a single glowing coal under the flask; the temperature should never exceed 45° or 50° (113 — 122° F.). The gas, after being dried by passing over chloride of calcium, may be collected by displacement in dry bottles; or if an aqueous solution be required, the gas may be passed into a series of Woulfe's bottles containing water. The action is at an end when the mixture in the flask becomes colourless. The chlorous acid thus obtained is mixed with carbonic acid resulting from the oxidation of the tartaric acid; but it is sufficiently pure for nearly all experiments that can be made with gas; and the process is much easier and attended with less danger than any other mode of preparing the same compound. Slight

percussions sometimes take place in the apparatus, but they never amount to dangerous explosions.—2. To obtain chlorous acid free from carbonic acid, arsenious acid may be substituted for the tartaric acid. Three parts of arsenious acid and 4 of chlorate of potash finely pounded and mixed with water to a fluid mass, are put into a flask like that used in the first method, and the flask filled up to the neck with a mixture of 12 parts nitric acid and 4 parts water: the mixture is then gently heated. The nitric acid must be pure and free from all admixture of hydrochloric or sulphuric acid; as either of these acids would cause the evolution of hypochloric acid and give rise to violent explosions. If these impurities are present in the nitric acid, the flask containing the mixture must be immersed in cold water for several hours, before being heated to liberate the chlorous acid.—3. By decomposing a salt of chlorous acid by means of a stronger acid. The most convenient salt for this purpose is the chlorite of lead. To obtain this salt, an aqueous solution of chlorous acid is saturated with baryta-water, the solution separated by filtration from carbonate of baryta (if any), and mixed with a perfectly neutral solution of nitrate of lead. Chlorite of lead is then precipitated in beautiful sulphur-yellow laminæ, which may be collected on a filter and washed. To obtain the acid from this salt, it is mixed to a pasty consistence with sulphuric acid diluted with an equal bulk of water, the mixture introduced into a small flask, and heated to a temperature between 40° and 50° degrees, fresh acid being added when necessary by means of a safety-tube. The gas is evolved with great facility, nothing being left in the flask but sulphate of lead and a small quantity of chlorous acid, which is retained in combination with the sulphuric acid, and cannot be expelled without the application of a degree of heat which would give rise to explosive decomposition. This is the only mode of obtaining chlorous acid perfectly pure; that which is produced by the second process always contains a small quantity of hypochloric acid. Whatever may be the process adapted for the preparation of chlorous acid, it is advisable to guard against accidents by surrounding the apparatus with a cage of wire-gauze or a cloth.

Properties. Chlorous acid is a gas of a rather dark greenish-yellow colour and strong pungent odour, irritating the air-passages like hypochloric acid. It bleaches litmus-paper and solution of indigo. Does not liquefy when cooled by a mixture of ice and salt. (Millon.) Condenses to a reddish liquid when exposed to intense cold. (Berzelius.) Specific gravity of the gas = 2·646. (Millon.)

	Calculation.		Millon.		Vol.	Sp. gr.	Vol.	Sp. gr.
Cl	35·4	59·60	60·15	Chlorine gas	2	4·9086	= $\frac{2}{3}$	1·6362
3O	24·0	40·40	39·85	Oxygen gas	3	3·3276	= 1	1·1092
ClO^3	59·4	100·00	100·00	Chlorous acid gas	3	8·2362	= 1	2·7454

(Cl^2O^3 = 2 . 221·33 + 3 . 100 = 742·66. Berzelius.)

Decompositions.—1. The gas, when heated to 57° (135° F.), explodes with moderate force, and is resolved into chlorine and oxygen. It explodes when brought in contact with most combustible bodies, as with sulphur, selenium, tellurium, phosphorus, and arsenic. Iodine absorbs it, forming a mixture of chloride of iodine and iodic acid. Bromine exerts no action upon it. Many metals, *e. g.* copper, lead, tin, antimony, silver, and iron-filings may be left for hours in the gas without producing

any effect; but mercury absorbs it completely. Caustic baryta and lime absorb the gas very slowly. Oxide of silver decomposes it instantly; the oxides of lead and copper and di-oxide of mercury, more slowly.

Combinations. *a.* With Water. *Aqueous Chlorous acid.* Water at ordinary temperatures absorbs about 5 or 6 times its volume of chlorous acid gas. The solution is green when it contains but little of the gas; deep golden yellow when saturated. A few bubbles of the gas are sufficient to give a perceptible colour to a pint of water—a tinting power which can only be compared to that of the soluble salts of chromic acid. The saturated solution has a caustic taste, and at 20° produces a yellow stain on the skin when placed in contact with it for a few seconds. The solution, like the gas, bleaches litmus and sulphate of indigo, just as chlorine and hypochlorous acid do; but the bleaching action of chlorous acid is not diminished by the addition of arsenious acid; whereas that of chlorine and hypochlorous acid is completely destroyed by it. If a few drops of a weak solution of chlorous acid (*e. g.* a solution containing its own volume of water) be dropped into a bottle containing air saturated with moisture, a thick white cloud rises from the bottom of the bottle, fills it, and continues to flow out at the mouth for upwards of half an hour. [For the cause of this phenomenon, *vid.* p. 318.]

2. The aqueous solution of chlorous acid converts mercury into oxychloride, and copper into chlorate and chloride; with zinc and lead, chloride and chlorite are at first produced; but, if the acid is in excess, the ultimate products are chloride and chlorate. On gold, platinum, and antimony, it exerts no action. The salts of the alkalis and earths in the state of aqueous solution are not altered by it; neither does it exert any action on the salts of zinc or on the dichloride or protochloride of mercury. Protochloride of tin it converts into bichloride. Mixed with solution of nitrate of manganous oxide, or of protochloride of manganese, it converts the metal into peroxide; similarly, with acetate of lead. With solution of subacetate of lead also it gives an immediate precipitate of peroxide. Ferrous salts are quickly converted by it into ferric salts. Nitrate, acetate, sulphate, and chloride of copper assume a green colour when mixed with it, but undergo no definite change. Salts of gold and platinum are not affected by it.

b. With Chloric acid. *c.* With Perchloric acid.

d. With Salifiable Bases. *Chlorites.* The chlorites of potassa, soda, baryta, and strontia, which are soluble, are formed by mixing the aqueous acid with the solutions of these alkalis. Combination does not take place immediately, on account of the feebleness of the affinity of chlorous acid for salifiable bases; at least an hour elapses before the odour of the acid is quite destroyed. The carbonates of potassa, soda, baryta, strontia, and lime, are not decomposed by chlorous acid. From the solutions of the alkaline chlorites, the lead and silver-salts, which are insoluble in water, may be obtained by double decomposition: the same method will doubtless be found applicable to the preparation of other insoluble chlorites. The normal salts of chlorous acid contain 1 atom of acid to 1 atom of base: those which are soluble are colourless, and taste like the acid itself; they likewise destroy vegetable colours. With potassa, soda, and baryta, chlorous acid also forms acid salts, which are red when in solution, but cannot be obtained in the solid state. Chlorous acid also forms basic salts which contain 2 atoms of base to 1 of acid. The chlorites are distinguished from the hypochlorites by the fact that their bleaching power is

not destroyed by a solution of arsenious acid in nitric acid. Chlorous acid is completely expelled from its combinations by carbonic acid, provided it is free to escape, and fresh quantities of carbonic acid are continually added: hence the chlorites are decomposed by exposure to the air. The chlorites of baryta, strontia, lead, and silver, are crystallizable. (*Vid.* Millon, *Ann. Pharm.* 46, 298; also Berzelius, *Traité*, I., 553.) ¶

C. Hypochloric Acid or Chloric Oxide. ClO^4.

Oxide of Chlorine, Peroxide of Chlorine, Stadion's *Teroxygenated Chlorine, Unterchlorsäure, Chlorige Säure, Acide Chloreux, Deutoxide de Chlore;—Chloric Oxide gas, Chloroxydgas, Gas deutoxide de Chlore.*

Preparation.—1. *In the gaseous state.* *a.* Stadion fuses 1 part of chlorate of potash in a small glass retort till it is reduced to a coherent mass—pours upon it, when cold, 4 parts of oil of vitriol—and heats it gradually in a water-bath, raising the temperature, in the course of three hours, from 12° to 100°.

$$3(KO, ClO^5) + 4SO^3 = 2(KO, 2SO^3) + KO, ClO^7 + 2ClO^4.$$

b. Davy mixes 30 grains of finely pounded chlorate of potash with a small quantity of oil of vitriol to the consistence of a paste, puts the mixture into a retort, and heats it gradually in a water-bath to which a little alchohol has been added to keep the temperature below 100°.—*c.* Gay-Lussac makes the paste with oil of vitriol diluted with one-half water. The first portions of chloric oxide which come in contact with the oil of vitriol and turn it brown, are evolved as soon as heat is applied; but if the heat becomes too strong and affects the gas itself more than the materials in the retort, explosion takes place; hence it is necessary to protect the face with a mask. The gas is collected over mercury; but the mercury is thereby partly converted into calomel; for the gas is always, especially towards the end of the operation, mixed with free chlorine and oxygen. (Stadion.) The gas-delivery tube should be surrounded with paper kept moist by a stream of cold water, to guard against explosion. Stadion's method with excess of oil of vitriol is the safest; but the gas which it yields always contains free oxygen, which remains behind when the chloric oxide is absorbed by water or mercury (and strongly cooled). *Soubeiran.* ¶ Millon adds finely-pounded chlorate of potassa by small portions at a time to sulphuric acid previously cooled by a mixture of ice and salt, stirring with a glass rod after each addition*. When a sufficient quantity has been added to render the acid somewhat viscid—about 15 or 20 parts of salt to 100 of acid—the liquid is poured through a funnel into a flask, care being taken not to soil the neck of the flask at the part which is touched by the cork, as otherwise explosion will very probably ensue. A larger proportion of oil of vitriol would decompose nearly all the chloric acid into chlorine and oxygen; and if a larger proportion of the chlorate were used, a violent explosion would probably take place soon after the mixture was put into the vessel. The flask is heated in a

* The purer the chlorate of potassa, the less danger is there of explosion. The tendency to violent explosions is much increased by the presence of mechanically-combined water, or of chloride of potassium. If any considerable quantity, as 500 or 600 grains, of the chlorate is to be used, the precaution of cooling the oil of vitriol is absolutely necessary, especially if the salt be impure. (Millon.)

water-bath, which must be slowly raised, by means of a single glowing coal placed under it, to a temperature not exceeding 20° (68 F°): at a later stage of the operation the heat may be gradually raised to between 30° and 60° (86°—104° F.): this rise of temperature makes no alteration in the composition of the gas evolved. The gas, which is heavy, may be collected in small bottles, by displacement; mercury absorbs it rather quickly. For safety, the apparatus should be surrounded with wire-gauze or with a linen cloth. The gas obtained by this method is purer than that which is yielded by either of the preceding, but still contains free chlorine and oxygen. The only way of obtaining the compound quite pure is to liquefy it by cooling. (Millon.)

2. *In the liquid state.* (I., 286.) Oil of vitriol is put into the shorter arm of the tube and chlorate of potassa into the longer arm—the latter is sealed—the oil of vitriol made to flow into it, and the whole left to itself for 24 hours. The longer arm is then heated to 38° (100° F.) and the shorter arm cooled to —18° (0° F.) (*Faraday;* Comp. Niemann, I., 287.) ¶ A much simpler mode of obtaining the liquid acid is to pass the gas, as it is evolved from a mixture of chlorate of potassa and sulphuric acid, into a tube sealed at one end and surrounded with a mixture of ice and salt. The tube should be changed at least every hour, as the liquid explodes with as much violence as chloride of nitrogen. (Millon.) ¶

Properties. The liquid oxide (or acid) is very fluid, of a deep yellow colour, and transparent: on opening the tube, it evaporates with great force. (Faraday.) Greenish yellow, and of specific gravity about 1·5. (Niemann.) Red, like bright-coloured chloride of sulphur; boils at 20°. (Millon.) For the tension and density of the gas, *vid.* I., 261, 279. The gas has a brighter yellow colour than chlorine. It does not bleach dry litmus paper, but destroys the colour of that which is moistened, without previously reddening it (Stadion; H. Davy): according to Berzelius, it first reddens litmus, and then bleaches it. Its odour is not so suffocating as that of chlorine (Stadion): it has an aromatic odour like that of burnt sugar, without any accompanying smell of chlorine. (H. Davy.)

Calculation.				Vol.	Sp. gr.
Cl	35·4	52·5	Chlorine gas	½	1·2272
4O	32·0	47·5	Oxygen gas	1	1·1093
ClO^4	67·4	100·0		1	2·3365

This is the composition of chloric oxide, according to Davy, Gay-Lussac, Soubeiran, and Millon: Stadion, on the contrary, regards it as a compound of 1 At. chlorine and 3 At. oxygen, or of 2 volumes of chlorine and 3 of oxygen condensed into 3 volumes.

Decompositions.—1. The gas remains unaltered in the dark; but in sun-light, it is gradually resolved into its elements. Sudden heating to 100°, the passage of an electric spark, or even agitation with mercury, produces an instantaneous decomposition, attended with vivid light and powerful detonation, and often with fracture of the containing vessel. Two measures of chloric oxide are thus resolved into 1 measure of chlorine and 2 of oxygen. (H. Davy; Gay-Lussac; Soubeiran.) According to Stadion, 3 vols. chloric oxide yield 2 vols. chlorine and 3 vols. oxygen.—2. A mixture of 3 measures of chloric oxide gas and about 8 measures of hydrogen explodes by the electric spark, producing water and hydrochloric acid. (Stadion.) Spongy platinum induces this decomposition at

ordinary temperatures. (Blundell, *Pogg.* 2, 216).—3. With ammoniacal gas, it suffers decomposition at ordinary temperatures. (Stadion.)—4. The gas explodes violently by contact with phosphorus (Stadion, H. Davy), and also with sulphur (Stadion) at ordinary temperatures.—5. Mercury absorbs the gas slowly, being itself converted into chloride of mercury and chlorate of mercurous oxide. (Stadion.) Nothing is left behind but the free oxygen previously mixed with the gas.

Combinations. *a.* With Water. ¶ *α. Hydrate of Hypochloric acid.* When water at 0° is poured upon the liquid acid, a solid yellow hydrate is formed, which cannot be liquefied without the loss of a great quantity of gas. The gas which escapes is undecomposed chloric oxide, but the last portions are retained by the water with great obstinacy, so that complete decomposition of the hydrate can only be effected by elevation of temperature or by passing a stream of another gas through the liquid. (Millon.) ¶

β. Aqueous Chloric oxide or *Aqueous Hypochloric acid.* Water absorbs more than 7 times its volume of chloric oxide gas (Stadion); more than 20 times its volume at 4°. (Millon.) The solution is of a deep yellow colour, tastes rough and caustic, but not acid; emits white fumes on exposure to the air, precipitates nitrate of silver in proportion as it undergoes decomposition; has the same odour and the same effect on litmus as the gas. In the dark it remains undecomposed; but when exposed to diffused daylight, it undergoes decomposition in the course of a few months, and by exposure to direct sunshine, in a few hours: the products of the decomposition are chloric acid and free chlorine. (Stadion.) The superior affinity of water for chloric acid causes the oxygen of the chloric oxide to combine with a portion only of its chlorine ($5ClO^4 = 4ClO^5 + Cl$). When the solution is heated in the dark, the gas escapes without leaving an acid in the liquid. (Soubeiran.)

b. With Salifiable Bases. *Hypochlorates?* According to Stadion and Sir H. Davy, chloric oxide gas, when passed through aqueous solutions of the alkalis, is immediately resolved into chloric acid and chlorine, so that a chlorate of the alkali and a chloride of the metal are produced:

$$6KO + 6ClO^4 = 5(KO, ClO^5) + KCl.$$

On the other hand, it appears from the experiments of Martens (*Ann. Chim. Phys.* 61, 293; also *J. pr. Chem.* 8, 264) that there really exist definite salts of hypochloric acid, which are resolved under the same circumstances as the hypochlorites, only not so easily, into chlorate and metallic chloride. When chloric oxide gas is passed into a solution of potassa, soda, or baryta, or into milk of lime, and in such quantity that the liquid still remains alkaline, a colourless solution is obtained which does not bleach litmus till an acid is added to it—does not contain a salt of chloric acid, except when highly concentrated,—and may be evaporated, at a gentle heat, or better in vacuo, to a dry crystalline mass. The liquid when heated with dilute mineral acids, or with the stronger vegetable acids, evolves chloric oxide gas, with brisk effervescence; whereas a mixture of chlorate and chloride similarly treated does not evolve a perceptible quantity of chloric oxide gas. When an alkaline solution is saturated with chloric oxide, a strongly bleaching liquid is produced which is no longer alkaline (any excess of chloric oxide, by which the solution is coloured brownish-yellow, escapes on exposure to the air). When this liquid is kept for some time at a temperature of 80° (176° F.),

or evaporated in vacuo at ordinary temperatures, the salt which it contains is resolved into chlorate and metallic chloride. Even carbonic acid passed through the liquid colours it yellow, and liberates a small quantity of chloric oxide; stronger acids decompose the salt completely, with brisk effervescence. Even when the hypochlorate is mixed with metallic chloride, it yields, when treated with acids, not chlorine but chloric oxide gas. (Martens.) ¶ Millon, in repeating the experiments of Martens, did not succeed in obtaining definite salts of hypochloric acid. To avoid rise of temperature and consequent decomposition, he made use of the liquid acid, adding it drop by drop to a solution of potassa; but he found that chlorate of potassa was always produced, however slowly the process was conducted. The solution however was not found to contain any metallic chloride; for, on the addition of nitrate of silver, it gave a yellow precipitate, which effervesced with nitric acid, and dissolved completely in boiling water, separating in yellow shining scales as the liquid cooled. The precipitate thus formed was chlorite of silver, AgO, ClO^3. From this it appears that when hypochloric acid is added to an alkaline solution, even in such a manner as not to occasion rise of temperature, it is resolved into chloric and chlorous acids:

$$2ClO^4 + 2KO = KO, ClO^5 + KO, ClO^3.$$

This decomposition is analogous to that which frequently takes place with hyponitric acid. (Millon.) ¶

D. Chloric Acid. ClO^5.

Hyper-oxymuriatic acid, Chlorsäure, Acide chlorique, Acide muriatique suroxygêne, Acidum chloricum.

Formation. 1. By exposing an aqueous solution of chloric oxide to the light. 2. By bringing chlorine in contact with water and a fixed alkali. (*Scheme* 34):

$$6KO + 6Cl = 5KCl, KO, ClO^5;$$

or *Scheme* 33: $6KO + 6Cl + 5HO = 5KO, HCl + KO, ClO^5$.

A mixture of metallic chloride and alkaline hypochlorite is always produced at first (p. 299); but the latter is resolved, especially by the action of light or heat and excess of chlorine, into metallic chloride and alkaline chlorate (p. 300). The earlier supposition of Berthollet, Robiquet, and others, that when the solution is largely diluted, a chloride of the alkali (that is, a mixture of metallic chloride and hypochlorite) is the principal product—and that when it is more concentrated, in which case the chlorate crystallizes out, the chief product is a salt of chloric acid—has not been confirmed; since, according to Gay-Lussac, a chlorate is formed by the action of heat and excess of chlorine, even when the liquid is very dilute.

Chloric acid is not known in the separate state.

	Calculation.		Gay-Lussac.	Chenevix.	Vauquelin.		Volume.
Cl	35·4	46·95	46·8	45·	35·	Chlorine gas	1
5O	40·0	53·05	53·2	55·	65·	Oxygen gas	2·5
ClO^5	75·4	100·00	100·0	100	100		

(Cl^2O^5 = 2 . 221·33 + 5 . 100 = 942·66. Berzelius.)

Combinations. *a.* With Water. *Aqueous Chloric acid. Prepara-*

tion.—1. An aqueous solution of chloric oxide is exposed to the sun's rays till the liquid becomes colourless, and the free chlorine afterwards expelled by gently heating it in the air. (Stadion; Gmelin.)—2. Chlorate of baryta is dissolved in water, and decomposed by dilute sulphuric acid. The acid liquid above the precipitated sulphate of baryta is separated by decantation; it should not be rendered turbid either by sulphuric acid or by chlorate of baryta. (Gay-Lussac.)—3. A hot aqueous solution of chlorate of potassa is mixed with an excess of hydrofluosilicic acid, and the acid liquid filtered, when cold, from the double fluoride of silicium and potassium; it is then evaporated at a temperature below 30°, and after a couple of days filtered through powdered glass. (Serullas.) Or the acid liquid mixed with finely-divided silica is left to evaporate, at a temperature below 30° (86° F.) in the air—or better in vacuo, over oil of vitriol or hydrate of potash—whereupon, the excess of hydrofluoric acid takes up a portion of the silica, and forms gaseous fluoride of silicium, which escapes: the chloric acid is then filtered from the remaining silica, and the residue washed with water, that nothing may be lost. (Berzelius.)

¶ Böttger decomposes chlorate of soda by means of oxalic acid: 7 parts of crystallized carbonate of soda and 7½ parts of tartaric acid are dissolved in 24 parts of boiling water; and to this is added a solution of 6 parts of chlorate of potash in 16 parts of water, likewise at a boiling heat, the whole being well stirred. As soon as the liquids are well mixed, the whole is removed from the fire and left to cool, so that the bitartrate of potash produced may settle to the bottom. The liquid is then passed through a double filter, the filtrate mixed with a saturated solution of oxalic acid (6 oxalic acid to 18 water) at a temperature not exceeding 56° (133° F.)—the whole briskly stirred—the vessel immersed in a freezing-mixture made of common hydrochloric acid and crystallized sulphate of soda, in order to facilitate the separation of the oxalate of soda, which is but slightly soluble, especially at low temperatures; and the liquid filtered again, to remove the oxalate of soda. The solution of chloric acid thus obtained is not absolutely pure, but sufficiently so for technical applications, such as the preparation of chlorate of baryta for pyrotechnic purposes. To obtain a pure and more concentrated acid, the liquid obtained by the preceding process may be saturated with freshly precipitated carbonate of baryta, the solution concentrated and left to crystallize, the crystals dissolved in a small quantity of water, and the baryta precipitated by sulphuric acid. (*Ann. Pharm.* 57, 138.) ¶

The aqueous solution of chloric acid is colourless, according to Gay-Lussac, Vauquelin, and Berzelius; but according to Serullas, it is yellowish when concentrated, even when not strong enough to precipitate nitrate of silver. It is not of an oily consistence, even when concentrated; it reddens litmus-paper, and then rapidly bleaches it (Serullas); the dilute acid reddens litmus, but bleaches it only after the lapse of several days. (Vauquelin.) The concentrated acid, especially when heated, has a pungent odour resembling that of nitric acid (Vauquelin; Serullas); the cold dilute acid is inodorous. (Gay-Lussac.) It has a very sour and astringent taste. (Vauquelin.) Does not precipitate salts of lead, mercury, or silver. (Vauquelin.)

The aqueous acid is not decomposed by light. (Gay-Lussac.) It is decomposed when heated to a temperature above 40°. When distilled, it yields nearly pure water at first, then aqueous perchloric acid, with disengagement of chlorine and oxygen gases, but no chloric acid. (Serullas.)

Hence, while one portion of the acid is resolved into its ultimate elements, another portion is converted into chlorine and perchloric acid.

$$7ClO^5 = 5ClO^7 + 2Cl.$$

Sulphurous acid decomposes aqueous chloric acid, forming sulphuric acid, and setting chlorine or hydrochloric acid free, according to the proportions employed:

$$5SO^2 + ClO^5 = 5SO^3 + Cl;$$
$$\text{and; } 6SO^2 + ClO^5 + HO = 6SO^3 + HCl.$$

Hydrosulphuric acid and aqueous chloric acid decompose each other, yielding water, hydrochloric acid, and sulphur, or water, hydrochloric acid, and sulphuric acid, according to the proportions used:

$$6HS + ClO^5 = 5HO + HCl + 6S;$$
$$\text{and: } 3HS + 2ClO^5 = 2HCl + HO + 3SO^3.$$

With hydrochloric acid, the products are chlorine and water.

$$5HCl + ClO^5 = 5HO + 6Cl.$$

(Gay-Lussac; Vauquelin.) Phosphorous acid and phosphuretted hydrogen gas likewise have a decomposing action on chloric acid. (Berzelius.) Alcohol and ether decompose it very rapidly. Bibulous paper folded several times together, saturated with strong chloric acid, and then squeezed out, burns with a vivid light, and emits a strong smell of chloric acid. (Serullas.) According to Gay-Lussac and Berzelius, zinc dissolves in the dilute acid, without decomposing it, hydrogen gas being evolved; according to Vauquelin, however, no hydrogen gas is evolved, but hydrochloric acid is formed. According to the author's own experiments, both these effects take place simultaneousyl. [For the decompositions by nitric acid with dexodizing agents, *vid.* pp. 305, 306.]

¶ *b.* With Chlorous Acid: *Chloro-chloric Acid,* $2ClO^5, ClO^3$. This compound is obtained by passing euchlorine, the gas obtained by the action of hydrochloric acid on chlorate of potash, through a series of *U*-tubes cooled by freezing mixtures, the first to 0°, the second to − 18°, (0° F.). Hydrochloric acid collects in the first, and a red liquid, which is the chloro-chloric acid, in the second and third: free chlorine escapes at the end of the apparatus. (Millon.)

Chloro-chloric acid, in appearance, strongly resembles liquid hypochloric acid: but it does not boil below 32° (89·6° F.), or explode below 70° (158° F.). It is soluble in water. The solution treated with caustic potash behaves like hypochloric acid, forming a chlorite and a chlorate; but the quantity of chlorate is twice as great as in the case of hypochloric acid, viz. 2 atoms of chlorate to 1 atom of chlorite. Hence the composition of the acid is determined to be $2ClO^5 + ClO^3 = Cl^3O^{13}$. (Millon.) ¶

c. With salifiable bases chloric acid forms the *Chlorates,* formerly called *Hyper-oxymuriates, Muriates suroxygénés.* These salts are obtained:—1. By mixing the aqueous acid with the salifiable base.—2. By dissolving zinc and some of the other metals in the dilute acid.—3. In company with metallic chlorides—from which they may be separated by crystallization and other means—by passing chlorine in excess through a caustic alkali, or alkaline carbonate, dissolved or diffused in water, and subsequently heating the liquid (p. 299.) Or a chloride of an alkali may be mixed with excess of hypochlorous acid, and exposed for a long time to the sun's rays or the heat of a water-bath, till the whole is converted into chlorate and metallic chloride; the hypochlorous acid may afterwards be recovered by distillation, and employed to act on fresh quantities of chloride. (Gay-Lussac.)

All chlorates are decomposed by heat—either giving off the 5 atoms of oxygen of the chloric acid, and the one atom of oxygen of the base, and leaving metallic chlorides (the alkali-metals, lead, silver, &c.), or—if the metal has a greater affinity for oxygen than for chlorine—evolving only the 5 atoms of oxygen belonging to the chloric acid, and leaving the metal in the state of oxide (the earth-metals). Many chlorates (at least the potash-salt) are resolved, at the temperature at which the evolution of oxygen commences, into metallic chloride and perchlorate. With combustible bodies, such as charcoal, phosphorus, sulphur, arsenic, antimony, metallic sulphides, sugar, &c., the chlorates explode—often indeed with the greatest violence—both on exposure to heat, and frequently also by a blow—in consequence of the oxygen, which is but feebly united with the chlorine, entering into a state of more intimate combination with the combustible body. The mixture of a chlorate with a combustible substance is often partially inflamed by oil of vitriol, probably, because that acid disengages chloric oxide, which readily gives up its oxygen to the inflammable substance. The inflammation with oil of vitriol does not take place in vacuo. (Hearder, *J. pr. Chem.* 26, 253.) Dry oxide of lead when heated with a dry chlorate, is converted into peroxide; sesquioxide of manganese, if an alkali be present, into manganic acid, &c. Oil of vitriol decomposes the chlorates, even at ordinary temperatures, into chloric oxide gas (which is partly absorbed by the oil of vitriol, forming a brownish-yellow solution, and is mixed with a small quantity of chlorine, and according to Sir H. Davy, $\frac{1}{20}$ of its volume of oxygen gas) and a mixture of sulphate and perchlorate. (*Vid.* p. 312.) Moreover, the heat disengaged frequently gives rise to sudden decomposition of the chloric oxide, producing decrepitation, detonation, and flashes of light. (Chenevix; Sir H. Davy; Stadion.) A mixture of equal parts of oil of vitriol and water, does not act perceptibly on chlorate of potash, at ordinary temperatures, unless chloride of potassium is present: in the latter case, chloric acid and hydrochloric acid are set free, which react on each other in atomic proportions, and yield equal measures of chloric oxide and chlorine gas. (Martens.) The solution of a chlorate in a moderate quantity of water, mixed cold with tincture of litmus, and then with oil of vitriol, discharges the colour of the litmus (a distinguishing character between the chlorates and the nitrates). (Vogel, Junior.) An aqueous solution of a chlorate, mixed with oil of vitriol, bleaches tincture of indigo, on the application of heat, in the same manner as the nitrates. (Orfila.) Nitric acid likewise decomposes the chlorates, evolving chloric oxide gas mixed with chlorine, and $\frac{1}{7}$ of its volume of oxygen gas. (H. Davy.) Chlorate of potash or soda, heated to dryness with nitric acid, evolves a mixture, containing 6 measures of chlorine to 13 measures of oxygen, and leaves 3 atoms of nitrate to one atom of perchlorate.

$$4(KO,ClO^5) + 3NO^5 = 3(KO,NO^5) + KO,ClO^7 + 3Cl + 13O.$$

(Penny, *Ann. Pharm.* 37, 203; also *J. pr. Chem.* 23, 296.) Hydrochloric acid when gently heated with a chlorate, evolves a mixture of 2 measures of chloric oxide gas and 3 measures of chlorine, in the form of euchlorine. (p. 304). Phosphoric, arsenic, oxalic, citric, and tartaric acids, with the aid of heat, produce similar results. Acetic and benzoic acids do not affect the chlorates. (Chenevix.) Hydrosulphuric acid, arsenious acid, and protochloride of tin, likewise produce no action on an aqueous solution of chlorate of potash, even when aided by heat. All chlorates are soluble

in water, the least soluble being the chlorate of potash; most of them dissolve so readily, that they deliquesce in the air. Their aqueous solutions do not precipitate the salts of any heavy metal, and consequently do not affect silver salts. This character affords the means of detecting a chloride mixed with a chlorate, and likewise distinguishes the chlorates from the bromates and iodates. The aqueous solutions of the chlorates do not discharge vegetable colours, unless a free acid is present. Many chlorates are soluble in alcohol.

E. Perchloric Acid.

Ueberchlorsäure, Oxidized Chloric acid, Acide perchlorique, Acide chlorique oxigéné, Acidum oxychloricum.

Formation.—1. In the circuit of the voltaic battery, chloric oxide evolves scarcely any gas at first; but after some hours, it gives off a small quantity of oxygen and chlorine at the positive pole, and hydrogen gas at the negative pole, the volume of the latter being more than double that of the oxygen disengaged at the positive pole. After some time, the liquid becomes colourless, and is converted into a solution of perchloric acid. (Stadion.)—2. When aqueous solution of chloric acid is distilled, perchloric acid passes over into the receiver. (Serullas.)—3. Oil of vitriol decomposes chlorate of potash at a gentle heat into chloric oxide gas, perchlorate of potash and bisulphate of potash. (Stadion, p. 309.) 4. Chlorate of potash when fused and kept for some time in a state of ebullition is resolved into oxygen gas and a mixture of chloride of potassium and perchlorate of potash, the latter of which amounts to about half the quantity of chlorate employed. (Serullas.)

Not known in the separate state.

Calculation according to Stadion.				Volume.
Cl	35·4	38·7	Chlorine gas	1
7O	56·0	61·3	Oxygen gas	3·5
ClO^7	91·4	100·0		

(Cl^2O^7 = 2 . 221·33 + 7 . 100 1142·66. Berzelius.)

Combinations. a. With Water. α. *Crystallized Perchloric acid.*—1. To prepare this substance, the aqueous acid is first concentrated by evaporation till it gives off abundant white fumes; it is then (in quantity not exceeding 10 grammes) mixed with between 4 and 5 times its volume of oil of vitriol, and the whole poured into a plain retort by means of a tube-funnel. The neck of the retort is then passed, without any cork or luting, into a bent tube, which is drawn out at the other end to a fine point, and kept cool by water: the mixture, which rapidly assumes a yellow colour, is kept in a state of moderate ebullition, till the drops which distil over no longer solidify, in consequence of their containing too much water. The greater part of the acid is decomposed, and escapes in the form of chlorine and oxygen gases; but a portion slowly runs into the tube, and there solidifies. (Serullas.)—2. 140 parts (one atom) of perchlorate of potash is distilled with 196 parts (4 atoms) of oil of vitriol at a gentle heat. The mass melts (which is not the case when only 2 atoms of oil of vitriol are used), and the acid solidifies in the neck of the retort,

which is kept cool for the purpose; the product, however, is but small. (Weppen, *Ann. Pharm.* 29, 318.) White, micaceous, or crystallized mass, or sometimes long, four-sided prisms with dihedral summits. Fuses at 45°. Emits white fumes in the air, and rapidly deliquesces. When the fused acid is dropped into water, each drop makes a hissing noise like red-hot iron. (Serullas.)

β. Aqueous Perchloric acid.—1. An aqueous solution of chloric acid is submitted to the action of a voltaic battery. (Vid. *Formation of Perchloric acid.*) (Stadion.)—2. Aqueous chloric acid is distilled, the receiver being changed during the process, and the heat increased till the whole has passed over. The first products are water and chlorine; afterwards a quantity of strong perchloric acid is obtained, amounting to one-third of the chloric acid originally employed. (Serullas.)—3. A mixture of 2 parts of perchlorate of potash with 2 parts of oil of vitriol and 1 part of water is heated in a tubulated retort to a temperature of 138° (280° F). Water distils over first, then aqueous perchloric acid, and lastly, a small quantity of chlorine, easily disengaged. The distilled acid is freed from sulphuric and hydrochloric acids by means of baryta-water and oxide of silver, and concentrated by careful evaporation. (Stadion.)—4. In a retort which is connected with a tube-funnel, then with a long tube, and then with a tubulated receiver immersed in cold water—without the use of any luting, or, at all events, only of asbestos—5 parts of perchlorate of potash are carefully heated with a mixture of 10 parts of oil of vitriol perfectly free from nitric acid, and 1 part of water, (if less oil of vitriol is employed, less acid is obtained). The mixture is never allowed to boil, and the heat is continued till the transparent fluid residue becomes colourless, and the drops of distillate follow each other very slowly, even when the temperature is somewhat raised. The distillate, which amounts to about 3 parts, of a density corresponding to 45° B. is purified from free chlorine and sulphuric acid by precipitating it with a saturated solution of sulphate of silver, filtering into a basin, and mixing it with such a quantity of freshly precipitated and well washed carbonate of baryta, that the whole of the sulphuric acid may be retained, and a small quantity of perchlorate of baryta formed. The solution is lastly distilled in a retort connected with the same apparatus as above, at a very slowly increasing heat. The greater part of the water passes over first, and afterwards concentrated perchloric acid, which is collected apart, and amounts to 1·5 parts. The distillation is carried nearly to dryness: by heating the residue longer, the perchlorates of silver and baryta would be decomposed, and evolve chlorine. (Nativelle, *J. Pharm.* 28, 498.)—5. Perchlorate of potash is briskly boiled with excess of hydrofluosilicic acid, whereupon gelatinous double fluoride of silicium and potassium separates as the liquid cools; the solution is then filtered, evaporated, cooled, refiltered, again evaporated, and lastly distilled. Serullas gives the preference to this method.—6. An aqueous solution of perchlorate of baryta is decomposed by an equivalent quantity of sulphuric acid, and the solution filtered. (O. Henry, *J. Pharm.* 25, 268; also *Ann. Pharm.* 31, 345.)

The dilute acid is best concentrated by careful evaporation in a retort, whereby a distillate is obtained consisting of nearly pure water: if the acid appears of a rose-colour, arising from the employment of chlorate of potash containing manganese, in its preparation, it must, when concentrated, be purified by distillation. (Serullas.)

The most concentrated acid has a specific gravity of 1·65; it is colourless, fumes slightly in the air, and boils at 200°. (Serullas.) It is oily,

like oil of vitriol, and has a density between 60° and 65° B. (Nativelle.) Perchloric acid is inodorous, has a strong and agreeably acid taste, reddens litmus without bleaching it, and volatilizes at about 138° without being decomposed. It is likewise unaffected by exposure to the sun's rays, and is not decomposed by hydrosulphuric, sulphurous, or hydrochloric acid. (Stadion.) Neither is it decomposed when heated with hydrochloric acid or with alcohol. Paper saturated with the strong acid does not take fire spontaneously, but when brought in contact with red-hot charcoal, it emits bright sparks accompanied by detonation. Paper held in the vapour of perchloric acid boiling in a tube, takes fire and burns vividly. The concentrated acid absorbs water from the air. (Serullas.)

b. With Chlorous Acid: *Chloro-perchloric Acid.* $2ClO^7, ClO^3$. Formed by the action of light on chlorous acid. When chlorous acid gas contained in a perfectly dry bottle is exposed to the direct rays of the sun, it is converted in a short time into perchloric acid, chlorine, and oxygen. The same decomposition takes place, though less quickly, in diffused daylight. But if the action of the light be modified by immersing the bottle containing the dry gas in water of the temperature of 20° (68° F.) no perchloric acid is formed, but in its stead a reddish-brown liquid, which runs down the sides of the vessel. The rays of the morning sun are more effective in producing this substance than those of the sun at noon. The liquid thus formed is the chloro-perchloric acid. It is decomposed by heat, but not explosively. In contact with moist air, it fumes so strongly that a few drops of it exposed in a room, the floor of which has been recently sprinkled with water, are sufficient to fill the whole space with a white mist. This is probably the cause of the dense fumes produced by dropping a dilute solution of chlorous acid into a bottle filled with moist air (p. 308), the chlorous acid being converted into chloro-perchloric acid by the influence of light. With caustic potash this acid forms 2 atoms of perchlorate and 1 atom of chlorate: hence its composition is $2ClO^7 + ClO^3 = Cl^3O^{17}$.

c. With Salifiable Bases. *Salts of Perchloric acid, Perchlorates.* Perchloric acid has a powerful affinity for salifiable bases. The salts are obtained either by mixing the acid and base, or by the methods described when speaking of the formation of the acid (*vid.* p. 316; also *Perchlorate of Potash* and *Perchlorate of Baryta*). Other salts of perchloric acid may be obtained by precipitating the potash-salt by hydrofluosilicates or the baryta-salt by sulphates. To obtain the deliquescent perchlorates in a crystallized state, Serullas leaves their alcoholic solution to evaporate in vacuo. The perchlorates require a greater heat to decompose them than the chlorates, but the decomposition takes place in a similar manner, the salts being resolved either into metallic chlorides and oxygen gas, or metallic oxides, oxygen, and chlorine. They explode violently on ignited charcoal; but, according to Stadion, the explosion is less violent with combustible bodies than that of the chlorates. Hydrosulphuric acid does not decompose their aqueous solutions. They are not decomposed by the strongest acids, not even by sulphuric acid, below 100°. (Stadion.) Consequently they do not assume a yellow colour on the addition of oil of vitriol or hydrochloric acid: this character distinguishes them from the chlorates. (Serullas.) All the perchlorates are soluble in water (Stadion), and likewise deliquescent, with the exception of the salts of ammonia, potassa, lead, and mercurous oxide (Serullas); the potash-salt is the most sparingly soluble of all. Hence perchloric acid precipitates perchlorate of potassa from the potash-salts and

a small quantity even from a solution of cream of tartar. (Sérullas.) A solution of a perchlorate does not precipitate the salts of any of the heavy metals. (Stadion.) The deliquescent salts are likewise soluble in alcohol; the potash-salt is insoluble in this menstruum.

That perchloric acid, notwithstanding the larger quantity of oxygen which it contains, is decomposed with less facility than chloric acid, when combined with water or with salifiable bases, is doubtless to be attributed to the fact of its being a stronger acid, and consequently retained by water and salifiable bases with greater force.

Chlorine and Hydrogen.

Hydrochloric Acid.

Muriatic acid, Hydrochlorsaure, Chlorwasserstoffsäure, Salzsäure, Kochsalzsäure, Seesalzsäure, Acide muriatique, Acide hydrochlorique, Acide chlorhydrique, Acidum salis s. muriaticum; and in the gaseous form: *Hydrochloric acid gas, Muriatic acid gas, Hydrochlorgas, Chlorwasserstoff gas, Gas acide muriatique, Gas acidum muriaticum.*—Found in the gaseous form in the vapours emitted from volcanos.

Formation. 1. When a mixture of equal volumes of chlorine and hydrogen is exposed to the sun's rays, it instantly explodes, with disengagement of light and heat, and is converted into hydrochloric acid gas; a feebler light, such as diffused daylight, induces slow combination. The two gases do not unite in the dark. (Gay-Lussac & Thénard.) In many instances, the combination which takes place on exposure to the sun, is not sudden but gradual: this was found to be the case by Bischof (*Kastn. Arch.* 1, 443, and in his *Lehrbuch*, 1, 93), and likewise by the author, especially in winter. In one experiment of Bischof's, the gaseous mixture did not explode on exposure to the sun's rays on a clear day in winter, even though the water surrounding the bottom of the receiver was heated as hot as the hand could bear it. On the other hand, explosion sometimes takes place in diffused daylight; as in an experiment of Silliman's, when the air was filled with thick snow-flakes. (*Sill. Amer. J.* 3, 343; also *Ann. Phil.* 19, 153; also *N. Tr.* 7, 2, 161.) The same thing happened in the author's hands, on a fine day in summer, as he was mixing the two gases in the open air under the shadow of a house, with the intention of subsequently removing the receiver into the sunshine. Liebig also (*Pogg.* 24, 281) found that the mixture could be exploded by the warmth of the hand without the influence of the sun's rays. A mixture of 1 volume of hydrogen with $1\frac{1}{2}$ vol. of chlorine explodes even in diffused daylight; a mixture of equal volumes, only in sunshine. (Döbereiner, *Pogg.* 25, 189.) Explosion in the sunshine takes place when the mixture is contained in a vessel of white glass; under dark blue glass, combination ensues, without explosion, in the course of a minute; under red glass, not at all, or but very slowly. (Seebeck.) On a bright day in summer, explosion occurred in an experiment of Bischof's, even under blue glass. A mixture of 1 volume of hydrogen, with between $1\frac{1}{2}$ and 2 volumes of chlorine, explodes when exposed to sun-light dimmed by clouds, also when contained in green medical bottles, and when exposed to the red light of early morning. A mixture of equal volumes of chlorine and hydrogen

explodes only in the direct rays of the sun, whether it be contained in colourless, in violet, or in blue glasses; the same mixture exposed to sunshine in green or red glasses, or to diffused daylight in colourless glasses, combines slowly; and when it is exposed to sunshine in orange-coloured glasses, no combination takes place. (Succow, *Pogg.* 32, 387.) According to Seebeck, the light from Indian white fire causes explosion; also, according to Drummond (*Pogg.* 9, 171), the light from lime ignited by the oxygen blow-pipe (p. 29): according to Bischof, however, explosion is not produced either by the light of Indian white fire, or by that of phosphorus burning in oxygen gas on each side of the gaseous mixture. Brande (*Ann. Chim. Phys.* 19, 205) produced combination, frequently attended with explosion, by the vivid light of charcoal ignited by a voltaic battery, but not by the light disengaged in the combustion of olefiant gas. Combination attended with violent explosion also takes place when a piece of brick heated to 150° or a burning body is introduced into the mixture, or when the mixture is transmitted through an ignited tube, or when an electric spark is passed through it. (Gay-Lussac & Thénard.) Sudden combination accompanied by a flashing light is produced by the electric spark, even when the mixture is 24 times diluted: 1 volume of the mixture diluted with 18 volumes of oxygen gas is still capable of taking fire in this manner. (H. Davy.) Blundell's statement that spongy platinum causes combination, is contradicted by Döbereiner and Faraday.

2. Chlorine, in consequence of its great affinity for hydrogen, decomposes all hydrogen compounds with the exception of hydrofluoric acid. It does not, however, decompose pure water in the dark, but slowly under the influence of light, even of diffused daylight, and more rapidly at a red heat (when a mixture of chlorine and aqueous vapour is passed through a red-hot porcelain tube), oxygen gas being set free (I., 129). If besides chlorine and water, there is likewise present a body which has some affinity for the oxygen of the water, such as boron, phosphorus, sulphur, selenium, iodine, phosphorous acid, sulphurous acid, metals, and organic substances (from the carbon they contain), the water is very readily decomposed, with oxidation of the third substance and formation of hydrochloric acid. Chlorine, even at ordinary temperatures, combines with the hydrogen of phosphuretted and arseniuretted hydrogen, hydrosulphuric acid, hydriodic acid, ammonia, and a great many organic compounds, namely, alcohol, ether, volatile oils, fats and resins; olefiant gas is decomposed by chlorine only at high temperatures; and marsh-gas, in the sun's rays, with explosion. (Gay-Lussac & Thénard.)

Preparation. 1. *In the gaseous form.* Common salt is mixed with an equal weight of oil of vitriol in a gas-generating apparatus, and the mixture gradually and gently heated. (*Scheme* 50.) The gas is received over mercury.

2. *In the liquid state.* (*Vid.* I., 286 and 287.)

Properties. In the liquid state it forms a colourless fluid, whose refractive power is equal to that of liquid carbonic acid. (Faraday.) Refracts light less powerfully than water, but more so than liquid carbonic acid. Is of a pale yellow colour when first formed, but becomes colourless on exposure to light, a proof that the colour is not essential to it, and probably arises from organic matter in the dust collected in the tube [from combustible matter in the sal ammoniac?]. (Niemann. *Br. Arch.* 36, 185;

Ann. Pharm. 1, 32.) (For the tension, specific gravity, and refractive power, *vid.* I., 261, 279, 95.) The gas is colourless. Fumes in moist air; has a peculiar, acid, and suffocating odour; is irrespirable; causes inflammation and itching of the skin. Reddens litmus strongly. Incombustible; extinguishes a burning taper, but the flame, before extinction, exhibits a greenish border.

Calculation.				Volume.	Sp. gr.
Cl	35·4	97·25	Chlorine gas	1	2·4543
H	1·0	2·75	Hydrogen gas	1	0·0693
HCl	36·4	100·00	Hydrochloric acid gas	2	1·2618

$$HCl = 6{\cdot}24 + 221{\cdot}33 = 227{\cdot}57. \quad \text{(Berzelius.)}$$

Decompositions.—1. Hydrochloric acid gas is decomposed by the electric spark; but the quantity decomposed never exceeds $\frac{1}{35}$ of the whole, for whatever time the passage of the sparks may be continued (W. Henry); for, on the other hand, the electric spark causes the separated gases to recombine (*vid.* p. 320). [For the decomposition of the aqueous acid by a current of electricity, *vid.* I., 455.]—2. A mixture of hydrochloric acid gas with $\frac{1}{4}$ vol. oxygen, yields water and chlorine gas when electrified; spongy platinum likewise, when gradually heated in this mixture, begins, at a temperature of 120°, to form water and liberate chlorine gas. (W. Henry.)—3. Hydrochloric acid and sulphurous acid do not act on each other in the state of solution, but when mixed perfectly dry in the gaseous form over mercury, they are resolved into water, chlorine, and sulphur. (Dumas, *Traité de Chim.* 1, 146.)—4. A mixture of 2 volumes of hydrochloric acid gas and 1 volume of hypochlorous acid gas is resolved, with disengagement of heat, into 1 volume of aqueous vapour and 2 volumes of chlorine gas. Hydrochloric acid gas acts in a similar manner on an aqueous solution of hypochlorous acid. (Balard.) By atoms:

$$HCl + ClO = HO + 2Cl;$$

By volume: 2 vol. hydrochloric acid gas contain 1 vol. chlorine and 1 vol, hydrogen; 1 vol. hypochlorous acid gas contains 1 vol. chlorine and $\frac{1}{2}$ vol. oxygen; 1 vol. hydrogen with $\frac{1}{2}$ vol. oxygen forms 1 vol. vapour of water; and 2 vol. chlorine are set free.—5. Metals, *viz.* potassium at ordinary temperatures, zinc (*Scheme* 9) tin, &c., with the aid of heat, and mercury, especially when electrolized, decompose 1 volume of hydrochloric acid gas into metallic chloride and a half volume of hydrogen gas.—6. Many salifiable metallic oxides (the earths excepted) act on hydrochloric acid gas, sometimes at ordinary, sometimes at rather elevated temperatures, producing water and anhydrous metallic chlorides. Under these circumstances, baryta and strontia become red hot, and lime disengages considerable heat. (Chevreul, *Ann. Chim.* 84, 285.) With the aqueous acid, only oxide of lead, the dioxides of copper and mercury and oxide of silver, form anhydrous chlorides; all other oxides yield solutions which may be regarded either as aqueous metallic chlorides, or as solutions of hydrochlorates of the oxides.—7. With metallic peroxides and some of the metallic acids, as with peroxide of manganese, peroxide of lead, chromic acid, &c., hydrochloric acid gas and aqueous hydrochloric acid yield chloride of the metal (or hydrochlorate of the oxide) and free chlorine:

$$MnO^2 + 2HCl = MnCl + 2HO + Cl.$$

Charcoal, phosphorus, and sulphur, do not act on hydrochloric acid at any temperature.

Combinations. a. With Water. *Aqueous Hydrochloric acid, Hydrochloric acid* in general, *Muriatic acid, Liquid Muriatic acid, Spirit of Salt, Acid Spirit of Salt, Fuming Spirit of Salt, Spiritus salis acidus, fumans.*

Hydrochloric acid gas condenses with the aqueous vapour of the air, forming clouds of aqueous hydrochloric acid; it is rapidly absorbed by ice, the ice melting at the same time; it is taken up still more rapidly by water, with considerable rise of temperature. Water absorbs not quite its own weight of hydrochloric acid gas: according to Sir H. Davy, water, at ordinary temperatures, absorbs 480 times its volume of the gas, and thereby acquires a specific gravity of 1·2109.

Preparation. In a glass vessel *a* (*App.* 50,) 8 parts of common salt are treated with a cold mixture of 13 parts of oil vitriol and 3 parts water, the vessel connected by means of three bent tubes—the second of which is a Welter's safety tube—with three Woulfe's bottles, which are immersed in water and surrounded at top with moistened bibulous paper. The first bottle *b* contains a very small quantity of water, the second *c*, a quantity of distilled water about equal to that of the common salt employed, and the third *d*, somewhat less. The vessel *a* is gradually heated in a sand-bath, or over an open fire, not quite to redness, till aqueous vapour is no longer given off. The acid which collects in the first bottle is diluted by the aqueous vapour which passes over at the end, and also contaminated with less volatile substances, such as selenium, chloride of arsenic, chloride of tin, and chloride of iron. The 8 parts of water in the second bottle are converted into about 13 parts of pure aqueous hydrochloric acid, of specific gravity 1·145; if the oil of vitriol contains nitric acid, the hydrochloric acid may be contaminated with free chlorine. The water in the third bottle absorbs the small quantity of hydrochloric acid which has not been taken up by the second, and in a subsequent operation may be further concentrated in the second bottle. When a still stronger acid is required, less water is introduced into the second bottle. Nothing is gained by heating the salt to decrepitation before using it. Undiluted oil of vitriol is not well adapted for the process, because it disengages a large quantity of hydrochloric acid as soon as it comes in contact with the salt, and even before the apparatus is connected; also because the mass is more liable to boil over when heated. With 1 atom of oil of vitriol to 1 atom of common salt (49 : 60 parts) the hydrochloric acid is far from being entirely evolved; the residue in this case is a mixture of bisulphate of soda and undecomposed common salt; with $1\frac{1}{2}$ atoms of oil of vitriol, about $\frac{4}{5}$ only of the hydrochloric acid is obtained; but with 2 atoms of oil of vitriol to 1 atom of common salt (98 : 60 parts) the decomposition is complete, and requires only a moderate temperature; moreover, the residue of bisulphate of soda remains semifluid even after cooling, and is therefore easily poured out. (*Vid.* Geiger, *N. Tr.* 3, 1, 462 and 4, 2, 462; Wittstein, *Repert.* 63, 225; Gregory, *Ann. Pharm.* 41, 375.)

Commercial Hydrochloric Acid is prepared on the large scale by heating a mixture of 1 atom of common salt with 1 atom of oil of vitriol or more dilute sulphuric acid in horizontal cast iron cylinders (glass retorts or cast iron or leaden boilers are not so much used). The gas evolved is generally conducted by means of bent tubes into a series of bottles containing water; or into a long, gradually rising, bricked channel, in which a small current of water is made to trickle down and meet the gas.

Impurities in aqueous hydrochloric acid, especially in the commercial acid:

Sulphurous acid: chiefly produced by the action of the sulphuric acid on the iron at a high temperature. The hydrochloric acid becomes turbid on mixing it with $\frac{1}{4}$ pt. of tin salt and 2 parts of water, often after some minutes only; the liquid appears yellow at first, then brown, and finally deposits brown sulphide of tin. (Girardin, *J. Pharm.* 21, 161; also *J. pr. Chem.* 6, 81.) Decolorizes sulphate of manganic oxide (Gay-Lussac) (an effect, however, which is produced when nitrous acid is present). Gives a precipitate of sulphur with sulphuretted hydrogen. Mixed with water and chloride of barium, and filtered from any sulphate of baryta that may be precipitated, it yields a fresh precipitate when boiled with nitric acid.

Sulphuric acid: Precipitates chloride of barium, after dilution.

Chlorine: When the oil of vitriol contains nitric acid or the common salt is contaminated with a nitrate. Yellow colour; odour; precipitation of sulphur from hydrosulphuric acid; solution of gold leaf; bleaching of solution of indigo.

Nitrous acid: from the same sources. Test with oil of vitriol and solution of ferrous sulphate (p. 181).

Chloride of arsenic: from arsenic contained in the sulphuric acid employed.

Wackenroder (*Repert.* 46, 225; 47, 337) found in a specimen of commercial hydrochloric acid, $\frac{1}{11934}$ of metallic arsenic; Dupasquier (*J. Pharm.* 27, 717) $\frac{1}{1835}$; Wittstein (*Repert.* 72,323), $\frac{1}{770}$; and Reinsch (*J. pr. Chem.* 24, 244), as much even as $\frac{1}{609}$. The arsenic is doubtless present in the acid in the very volatile form of chloride of arsenic. (Dupasquier.) Hence when hydrochloric acid is prepared from common salt and sulphuric acid containing arsenic, in the above-described Woulfe's apparatus, even the hydrochloric acid in the second bottle *c* will be found to contain arsenic, unless the first bent tube is made to dip under the water in the first bottle *b*. (Wackenroder.) Even when commercial hydrochloric acid contaminated with arsenic is heated in a retort connected with an empty tubulated receiver, from which a bent tube conveys the hydrochloric acid gas into water, the aqueous acid obtained is still found to contain arsenic. (Dupasquier.) Arseniuretted hydrochloric acid yields arsenical spots with Marsh's apparatus; covers mercury with a brown film (Wittstein); leaves a residue of arsenic acid when evaporated to dryness with nitric acid, though when evaporated alone it leaves no residue (Dupasquier); and yields yellow flakes of sulphide of arsenic, when treated with hydrosulphuric acid. If the arsenic be precipitated by sulphuretted hydrogen and the acid distilled without removing the precipitate, the distillate still contains arsenic, because, on applying heat, the sulphide of arsenic is again decomposed by the concentrated hydrochloric acid. (Dupasquier.) For this reason, the hydrochloric acid must be filtered through asbestos, after the arsenic has been completely precipitated by sulphuretted hydrogen (Dupasquier)—or diluted with an equal volume of water, before being treated with sulphuretted hydrogen, and afterwards filtered through paper. (Wackenroder, Dupasquier.) From the paper, however, the acid takes up organic matter, which imparts a yellow colour to it on boiling, and must afterwards be separated by distillation. (Wittstein.) It is better, therefore, in the preparation of hydrochloric acid, to employ sulphuric acid free from arsenic.

Bichloride of Tin: passes at the commencement of the distillation into

the first Woulfe's bottle, if the oil of vitriol contains binoxide of tin. Hydrochloric acid which contains this impurity gives with hydrosulphuric acid, after several days, a brown precipitate which yields a globule of tin before the blowpipe. (Berzelius, *Pogg.* 33, 24.)

Soda, Lime, and other *fixed substances* remain behind when the hydrochloric acid is evaporated to dryness.

Aqueous hydrochloric acid is colourless, when perfectly free from sesquioxide of iron, chlorine, or organic matter; but either of these impurities imparts a yellow colour to it. At a temperature below the freezing point of mercury, it solidifies to a mass of the consistence of butter.

Refractive power of Aqueous Hydrochloric acid of different densities; that of Water = 1.

Sp. gr.	Refract. power.	Sp. gr.	Refract. power.
1·055	1·053	1·121	1·121
1·087	1·088	1·146	1·138
		1·177	1·180

Hence the refractive power of the acid varies directly as its density. (Crighton, *Quart. J. of Sc.* 17, 182; also *Schw.* 32, 328.) The concentrated acid fumes in the air; boils at a temperature which is lower as the strength is greater, and gives off a portion of its hydrochloric acid gas; a more dilute acid, on the contrary, boils at a higher temperature than water. A strong acid is rendered weaker by boiling, a weak acid stronger, so that the ultimate residue is of the same strength in both cases. (Dalton.) Hydrochloric acid, saturated at 0° has a specific gravity of 1·2109, and appears to contain one atom of hydrochloric acid to 6 atoms of water = 6HO, HCl. (Kane.) The acid whose boiling point is constant, contains 20 per cent. of hydrochloric acid gas, and consequently one atom of acid to 16 atoms of water. The specific gravity of its vapour is 0·691; consequently 9 volumes are composed of one volume of hydrochloric acid gas and 8 volumes of aqueous vapour united without condensation. (Bineau, *Ann. Chim. Phys.* 68, 422.) Aqueous hydrochloric acid has a very sour taste, and a slight corrosive action. It has a pungent and purely acid odour, but when contaminated with iron, it smells like saffron.

Aqueous hydrochloric acid is miscible with peroxide of hydrogen, and absorbs carbonic acid gas in small quantity.

Percentage of Hydrochloric Acid Gas in Aqueous Hydrochloric Acid.

According to Edm. Davy, at 25° (77°F.)				According to Kirwan & Dalton.		
Sp. gr.	Acid per cent.	Sp. gr.	Acid per cent.	Sp. gr.	Acid per cent.	Boiling point.
1·21	42·43	1·11	22.22	1·199	34·01	49°?
1·20	40·80	1·10	20·20	1·181	31·09	65
1·19	38·38	1·09	18·18	1·166	28·29	76
1·18	36·36	1·08	16·16	1·154	26·57	87
1·17	34·34	1·07	14·14	1·144	24·84	100
1·16	32·32	1·06	12·12	1·136	23·25	103
1·15	30·30	1·05	10·10	1·127	21·06	105
1·14	28·28	1·04	8·08	1·121	20·74	109
1·13	26·26	1·03	6·06	1·094	16·08	111
1·12	24·24	1·02	4·04	1·075	13·16	109
		1·01	2·02	1·064	11·16	107
				1·047	8·62	105
				1·035	6·92	104
				1·018	3·52	102
				1·009	1·86	101

Percentage of Hydrochloric Acid Gas in Aqueous Hydrochloric Acid.

According to A. Ure (*Dictionary of Practical Chemistry*, 99.)

Sp. gr.	Per cent.	Sp. gr.	Per cent.	Sp. gr.	Per cent.	Sp. gr.	Per cent.
1.2000	40·777	1·1515	30·582	1·1000	20·288	1·0497	10·194
1·1982	40·369	1·1494	30·174	1·0980	19·980	1·0477	9·768
1·1964	39·961	1·1473	29·767	1·0960	19·572	1·0457	9·379
1·1946	39·554	1·1452	29·359	1·0939	19·165	1·0437	8·971
1·1928	39·146	1·1431	28·951	1·0919	18·757	1·0417	8·563
1·1910	38·738	1·1410	28·544	1·0899	18·349	1·0397	8·155
1·1893	38·330	1·1389	28·136	1·0879	17·941	1·0377	7·747
1·1875	37·923	1·1369	27·728	1·0859	17·534	1·0357	7·340
1·1859	37·516	1·1349	27·321	1·0838	17·126	1·0337	6·932
1·1846	37·108	1·1328	26·913	1·0818	16·718	1·0318	6·524
1·1822	36·700	1·1308	26·505	1·0798	16·310	1·0298	6·116
1·1802	36·292	1·1287	26·098	1·0778	15·902	1·0279	5·709
1·1782	35·884	1·1267	25·690	1·0758	15·494	1·0259	5·301
1·1762	35·476	1·1247	25·282	1·0738	15·087	1·0239	4·893
1·1741	35·068	1·1226	24·874	1·0718	14·679	1·0220	4·486
1·1721	34·660	1·1206	24·446	1·0697	14·271	1·0200	4·078
1·1701	34·252	1·1185	24·058	1·0677	13·363	1·0180	3·670
1·1681	33·845	1·1164	23·650	1·0657	13·456	1·0160	3·262
1·1661	33·437	1·1143	23·242	1·0637	13·049	1·0140	2·854
1·1641	33·029	1·1123	22·834	1·0617	12·641	1·0120	2·447
1·1620	32·621	1·1102	22·426	1·0597	12·233	1·0100	2·039
1·1599	32·213	1·1082	22·019	1·0577	11·825	1·0080	1·631
1·1578	31·805	1·1061	21·611	1·0557	11·418	1·0060	1·224
1·1557	31·398	1·1041	21·203	1·0537	11·010	1·0040	0·816
1·1536	30·990	1·1020	20·796	1·0517	10·602	1·0020	0·408

b. With Salifiable bases. *Hydrochlorates.* (Vid. *Metallic Chlorides.*)
c. With Organic compounds, as with alcohol, volatile oils, &c.

BICHLORIDE OF HYDROGEN. Concentrated hydrochloric acid treated with peroxide of lead at ordinary temperatures, yields chloride of lead, water, and free chlorine.

$$PbO^2 + 2HCl = PbCl + 2HO + Cl.$$

But if the peroxide is added in small successive portions to hydrochloric acid contained in a thin tube, and surrounded with a freezing mixture, chloride of lead is precipitated without effervescence, and a yellow liquid obtained which probably contains bichloride of hydrogen.

$$PbO^2 + 3HCl \quad PbCl + 2HO + HCl^2.$$

The liquid if left to itself, continues to evolve chlorine for several days; with zinc or mercury it yields chloride of the metal and free hydrochloric acid; it exhibits bleaching properties, and disengages carbonic acid gas when treated with oxalic acid. The liquid however contains lead in solution, which, on the addition of water, separates in the form of peroxide; hence it probably contains $PbCl^2$. (Millon, *J. Pharm.* 28, 299.)—[May not the liquid contain hypochlorite of lead?]

$$2PbO^2 + 2HCl = PbCl + 2HO + PbO, ClO. \quad (Gm.)$$

Chlorine and Carbon.

Charcoal, even at a red heat, has no action on chlorine, except indeed that a small quantity of hydrochloric acid is at first produced from the hydrogen contained in the charcoal. (Gay-Lussac, Thénard, H. Davy.)

Chloride of Carbon and *Oil of Olefiant Gas* will be described among *Organic Compounds*.

Phosgene. COCl.

Chlorocarbonic oxide, Chlor-kohlenoxyd, Acide chloroxycarbonique, Phosgene gas, Gas chloroxycarbonique.

Formation and *Preparation.*—1. When chlorine gas and carbonic oxide, both perfectly dry, are mixed in an exhausted receiver, no action takes place in the dark; but in diffused daylight, combination ensues in the course of 24 hours, and in sunshine in a few minutes, a new gas being formed which occupies half the volume of the original mixture. (J. Davy.)—2. Carbonic oxide gas passed over ignited chloride of lead or chloride of silver, reduces the metal and yields phosgene gas. (Göbel, *J. pr. Chem.* 6, 388.)

Properties. Colourless gas (for the specific gravity and refractive power, *vid.* p. 279); does not fume in the air; has a more unpleasant and suffocating odour, even than chlorine gas; excites tears; reddens moistened litmus-paper. (J. Davy.)

Calculation, according to J. Davy.				Volume.	Sp. gr.
CO	14·0	28·34	Carbonic oxide gas	1	0·9706
Cl	35·4	71·66	Chlorine gas	1	2·4543
CO, Cl	49·4	100·00	Phosgene gas	1	3·4249

(CO, Cl^2 = 176·44 + 2 . 221·33 = 619·10. Berzelius.)

This compound cannot well be regarded as carbonic acid in which 1 At. O is replaced by 1 At. Cl, inasmuch as 1 volume of phosgene gas condenses 2 volumes of ammoniacal gas, whereas 1 volume of carbonic acid gas condenses at most 1 volume of ammoniacal gas; it is probably therefore carbonate of bichloride of carbon = CO^2,CCl^2. (H. Rose, *Pogg.* 52, 77.) On the other hand, however, it must be observed that the compound CCl^2 is not known to exist. [It has since been discovered by Regnault (W.)].

Decompositions.—1. Cannot be made to explode by the electric spark when mixed either with oxygen or with hydrogen gas alone; but if mixed at the same time with half its volume of oxygen and an equal volume of hydrogen, it explodes violently by the electric spark, yielding hydrochloric acid and carbonic acid. Water rapidly produces the same decomposition (slowly, however, according to Serullas, *Ann. Chim. Phys.* 22, 187).—2. Potassium causes the entire disappearance of the gas, one portion of the metal absorbing the chlorine, and another portion the oxygen of the carbonic oxide, without evolution of light or heat: the products are chloride of potassium, potash, and carbon.—3. Arsenic, antimony, zinc, and tin, when introduced into the gas in a heated

state, are converted, without incandescence, into chlorides, and a quantity of carbonic oxide gas is separated equal in volume to the decomposed phosgene.—4. Oxide of zinc heated in phosgene gas, removes the chlorine from the carbonic oxide, and replaces it with its own oxygen, forming chloride of zinc and carbonic acid gas, of the same volume as the original phosgene. Oxide of antimony produces chloride of antimony and antimonious or antimonic acid, and leaves carbonic oxide gas. Phosphorus and sulphur sublimed in phosgene gas, do not produce any change. (J. Davy.)

Combinations. *a.* With chloride of sulphur.—*b.* With ammonia.—*c.* With chloride of arsenic.—*d.* With alcohol.

Chlorine and Boron.

Chloride of Boron. BCl^3.

Chlorboron, Chlorure de Bore; in the gaseous form: *Chloroboric gas.*

Formation.—1. Recently prepared boron, not previously heated in vacuo, takes fire spontaneously in chlorine gas, and burns with great splendour; after being heated, however, it inflames at high temperatures only. (Berzelius.)—2. Chlorine gas brought in contact with an ignited mixture of charcoal and boracic acid, forms chloride of boron and carbonic oxide. (Dumas.)

$$BO^3 + 3C + 3Cl^3 = BCl^3 + 3CO.$$

The resulting gaseous mixture contains 3 volumes of carbonic oxide to 2 volumes of chloride of boron. (Dumas.)

Preparation.—1. Dry chlorine gas is passed over perfectly dry boron ignited in the broad part of a tube; the gas is collected over mercury; and the free chlorine removed by agitation with the mercury. (Berzelius.)—2. A mixture of charcoal and boracic acid is ignited in a glass or porcelain tube for an hour, in order to expel every trace of moisture, and perfectly dry chlorine afterwards passed over the ignited mixture. Even the stoppers must be perfectly dry; if any moisture is present, hydrochloric acid is formed, and boracic acid deposited in the tube. (Dumas.) From the gaseous mixture collected over mercury, the carbonic oxide cannot be removed.

Properties. Colourless gas, having a sour, pungent odour arising from the formation of hydrochloric acid; emits dense white fumes in the air as abundantly as gaseous fluoride of boron. (Berzelius.)

Calculation.				Vol.	Sp. gr.		Vol.	Sp. gr.
B	10·8	9·23	Vapour of Boron?	1	0·7487	=	½	0·3743
3Cl	106·2	90·77	Chlorine gas	3	7·3629	=	1½	3·6815
BCl^3	117.0	100·00	Chlorboracic acid gas	2	8·1116	=	1	4·0558

(BCl^6 = 136·2 + 6 . 221·33 = 1464·18. Berzelius.)

The gas is rapidly but not instantaneously absorbed by water, which converts it into hydrochloric and boracic acids; when a small quantity of water is used, the latter is deposited on the surface in the solid form.

(Berzelius.) With a small quantity of water, chloride of boron forms a solid hydrate, which, at a low red heat is decomposed by hydrogen gas into hydrochloric acid and boron. (Dumas; *comp.* Liebig, *Schw.* 47, 117.) Chloride of boron combines with ammonia, and is likewise absorbed by alcohol. (Berzelius.)

Chlorine and Phosphorus.

A. Terchloride of Phosphorus. PCl^3.

Dreifach-chlorphosphor, Chlorphosphor im Minimum, Protochlorure de Phosphore.

Formation. 1. Phosphorus takes fire in chlorine gas at ordinary temperatures, burning with a pale green light and emission of sparks, and forming terchloride or pentachloride of phosphorus, according to the proportions in which the two elements are brought together.—2. Phosphorus withdraws chlorine from mercury.—3. Terchloride of phosphorus appears also to be formed in small quantity, when glacial phosphoric acid is ignited with common salt. (Gay-Lussac & Thénard.)

Preparation. Chlorine gas slowly evolved in the flask *a* (*App.* 52), is made to pass, first into an empty bottle *b*, artificially cooled, then through a tube *c* filled with chloride of calcium, and lastly, into the tubulated retort *d*, from which the terchloride, as it forms, distils over into the receiver *e*.—2. Vapour of phosphorus is passed over heated dichloride or protochloride of mercury. Phosphorus is placed at the closed end of a tube, chloride of mercury in the middle, and the open end of the tube is connected with a receiver kept at a low temperature. (H. Davy.) According to Berzelius and Dulong, the compound, as obtained by either of the preceding methods, may be purified from excess of phosphorus by a second distillation; according to Davy, however, the purification thus attained is not complete.

Properties. Transparent and colourless; very fluid; specific gravity = 1·45. (H. Davy.) Boils at 78° (172·4 F.) when the barometer stands at 30 inches (Dumas); at 78·34° (173° F.) when the barometer stands at 29·83 inches. (Pierre.) Specific gravity of the vapour (I., 279). Does not conduct electricity. Forms white fumes in the air; has a pungent odour, like that of hydrochloric acid; does not redden dry litmus paper. (H. Davy.)

	Calculation.		H. Davy. earlier.	H. Davy. later.	Berzelius.
P	31·4	22·82	23	26·3	23
3Cl	106·2	77·18	77	73·7	77
PCl^3	137·6	100·00	100	100·0	100

	Vol.	Sp. gr.		Vol.	Sp. gr.
Vapour of phosphorus	1	4·3539	=	¼	1·0885
Chlorine gas	6	14·7258	=	1½	3·6814
Vapour of terchloride of phosphorus	4	19·0797	=	1	4·7699

(PCl^3 = 196·14 + 3 . 221·33 = 860·13. Berzelius.)

Decompositions.—1. The vapour burns in the flame of a candle. (H.

Davy.)—2. With water, it gradually forms hydrochloric and phosphorous acid, the decomposition being attended with rise of temperature. (H. Davy.)

$$PCl^3 + 3HO = PO^3 + 3HCl.$$

3. Iron filings brought in contact with it at a red heat produce chloride and phosphide of iron. (Gay-Lussac & Thénard.) Potassium burns in its vapour with a dazzling light. (H. Davy.)—4. With phosphuretted hydrogen gas, it forms hydrochloric acid and yellow phosphorus, which soon turns red on exposure to light. (H. Rose, *Pogg.* 24, 307.)

$$PCl^3 + PH^3 = 3HCl + 2P.$$

Similarly with hydrosulphuric acid gas, it forms hydrochloric acid and tersulphide of phosphorus, with evolution of heat. (Serullas, *Ann. Chim. Phys.* 42, 32.)

$$PCl + 3HS = PS^3 + 3HCl.$$

Terchloride of phosphorus when heated is capable of dissolving a small additional quantity of phosphorus. The solution, when exposed to the air, deposits a film of phosphorus; paper moistened with it takes fire as soon as the liquid has evaporated by exposure to the air. (H. Davy.) The solution remains clear in the dark, but deposits hydrated phosphoric oxide when exposed to daylight; in direct sunshine the red oxide is quickly deposited. (Leverrier, *Ann. Chim. Phys.* 65, 259.) With water it forms hydrochloric and phosphorous acid, and deposits colourless, transparent phosphorus, which obstinately retains chlorine. (Berzelius.)

Terchloride of phosphorus combines with ammonia.

B. Pentachloride of Phosphorus. PCl^5.

Fünffach-chlorphosphor, Chlorphosphor im maximum, Deutochlorure de Phosphore.

Formation and Preparation.—1. By burning phosphorus in excess of dry chlorine gas—most conveniently, in a Woulfe's bottle or a tubulated retort (*App.* 52) not heated.—2. By exposing terchloride of phosphorus to chlorine gas.

Properties. Snow-white powder, which volatilizes much below 100°; may be fused under increased pressure; and afterwards, on cooling, crystallizes in transparent prisms. Does not conduct electricity. Fumes in the air; reddens dry litmus paper. (H. Davy.) Berzelius attributes this effect to the formation of hydrochloric and phosphoric acid by the combination of the phosphorus with the hydrogen and oxygen of the paper.

	Calculation.		H. Davy.	Dulong.	Berzelius.
P	31·4	15·07	13	15·4	15·31
5Cl	177·0	84·93	87	84·6	84·69
PCl^5	208·4	100·00	100	100·0	100·00

	Vol.	Sp. gr.		Vol.	Sp. gr.
Vapour of phosphorus	1	4·3539	=	$\frac{1}{6}$	0·7256
Chlorine gas	10	24·5430	=	$\frac{5}{6}$	4·0905
Vapour of pentachloride of phosphorus	6	28·8969	=	1	4·8161

(PCl^5 = 196·14 + 5 . 221·33 = 1302·79. Berzelius.)

Decompositions.—1. Begins to burn when put into the flame of a candle.

On passing its vapour mixed with oxyen gas through a red-hot porcelain tube, phosphoric acid and chlorine gas are obtained. (H. Davy.)—2. With water it forms phosphoric and hydrochloric acid, great heat being evolved. (H. Davy.) *Sch.* 40:

$$PCl^5 + 5HO = PO^5 + 5HCl.$$

—3. Pentachloride of phosphorus and phosphuretted hydrogen form hydrochloric acid and terchloride of phosphorus, or hydrochloric acid and phosphorus, according as the quantity of the latter compound is smaller or greater;

$$3PCl^5 + PH^3 = 4PCl^3 + 3HCl$$

and: $$3PCl^5 + 5PH^3 = 8P + 15HCl.$$

—4. With dry hydrosulphuric acid gas, the products are hydrochloric acid and chlorosulphide of phosphorus. (Serullas.)

$$PCl^5 + 2HS = PS^2Cl^3 + 2HCl.$$

—5. Potassium heated in its vapour burns with great rapidity and brilliancy. (H. Davy.)—6. With metallic oxides, it forms chloride of the metal and phosphate of the oxide. (H. Davy.)

Pentachloride of phosphorus forms a definite compound with ammonia.

¶ C. Oxychloride of Phosphorus. PCl^3O^2.

Formation and Preparation. When pentachloride of phosphorus is left to stand in an imperfectly stopped bottle or a long-necked flask, in which is also placed a tube filled with water, it gradually liquefies and evolves a considerable quantity of hydrochloric acid:

$$PCl^5 + 2HO = PCl^3 O^2 + 2HCl.$$

On distilling the product after all the pentachloride has disappeared, the hydrochloric acid passes over first, and afterwards, when the temperature reaches 110° (230° F.), the oxychloride.

Properties. Colourless liquid, of high refracting power, and having a pungent odour like that of terchloride of phosphorus. Specific gravity =1·7, at the temperature of 12° (53·6° F.). Specific gravity of the vapour 5·4.

	Calculation.		Wurtz.
P	31·4	20·44	20·50
3Cl	106·2	69·14	68·95
2O	16·0	10·42	10·55
PCl^3O^2	153·6	100·00	100·00

	Vol.	Sp. gr.		Vol.	Sp. gr.
Vapour of phosphorus	1	4·3539	=	¼	1·0885
Chlorine gas	6	14·7258	=	1½	3·6814
Oxygen gas	2	2·2186	=	¼	0·5546
Vapour of oxychloride of phosphorus	4	21·2983	=	1	5·3245

(PCl^3O = 196·14 + 3 . 221·33 + 100 = 960·13. Berzelius.)

Oxychloride of phosphorus emits white fumes when exposed to the air; it is decomposed by water, the products being phosphoric and hydrochloric acid, (reciprocal affinity):

$$PCl^3O^2 + 3HO = PO^5 + 3HCl.$$

Not decomposed by hydrosulphuric acid. Forms a white solid compound with ammonia. (Wurtz, *N. Ann. Chim. Phys.* 20, 472.) ¶

HYDROCHLORATE OF PHOSPHURETTED HYDROGEN. Known in union with the compound of chloride of titanium and phosphuretted hydrogen. Hydrochloric acid gas and phosphuretted hydrogen gas do not act on each other perceptibly, even in sunshine; moreover, the hydrochloric acid may be absorbed from the mixture by water and even by borax. But when a mixture of these two gases, prepared with the less inflammable phosphuretted hydrogen, is passed through aqueous ammonia, the unabsorbed gas is found to be spontaneously inflammable (H. Rose). This circumstance is in favour of the supposition that the gases are really combined, but without condensation, just as hydriodic and hydrobromic acid combine with phosphuretted hydrogen without condensation. The difference between them is that the hydrochloric acid compound is much more elastic, not undergoing liquefaction even at $-12°$. (Bineau, *Ann. Chim. Phys.* 68, 431.)

CHLORINE AND SULPHUR.

A. CHLORIDE OF SULPHUR.

Sulpho-muriatic acid, Chlorschwefel, Schwefelsalzsäure Salzsaures Schwefeloxyd, Chlorure de Soufre.—*Formation.* Pounded sulphur absorbs chlorine gas even at ordinary temperatures, the combination being attended with development of heat: the absorption is accelerated by subliming the sulphur in the gas. Berthollet's statement, that burning sulphur continues to burn when immersed in chlorine gas, appears to be unfounded.

a. DICHLORIDE OF SULPHUR. S^2Cl.

Halb-chlorschwefel, Chlorschwefel im Minimum, Protochlorure de Soufre.

Preparation. Dry chlorine gas is passed through washed and dried flowers of sulphur, till the sulphur is neally all dissolved. The liquid is then decanted, and freed by distillation at a gentle heat from the excess of sulphur which is dissolved in it (H. Rose). Dumas rectifies this first distillate a second time, because part of the excess of sulphur generally passes over with it. Marchand repeats the rectification till the boiling point of the liquid becomes fixed at 109° (228·2° F.). For passing the chlorine through the sulphur, *App.* 52 may be used, substituting for the retort *d* and receiver *e*, two Woulfe's bottles to contain the sulphur, these bottles being surrounded with cold water and connected by a bent tube.—¶ 2. Chlorine gas, previously washed and dried, is passed into a tubulated retort (*App.* 52) in which sulphur is sublimed by the application of a gentle heat: the chloride of sulphur distils over and may be condensed in a receiver surrounded by cold water; it must afterwards be rectified to free it from excess of sulphur. (Mitscherlich, *Lehrb.* I., 67.) ¶—3. A mixture of 1 part sulphur with 9 parts protochloride of tin, or 8·5 parts protochloride of mercury is subjected to distillation. (Berzelius.)

Properties. Brownish yellow, oily liquid of specific gravity 1·687 (Dumas), 1·686 (Marchand). Boils at 138° (280·4° F.) *Dumas*; begins to boil at 134°, but the boiling point soon rises to 139°, and then remains constant. (Marchand.) Specific gravity of the vapour (I., 279). Fumes strongly in the air; has a disagreeable, suffocating odour, something like that of sea-weed; its vapour excites tears; its taste is sour, hot, and bitter. Reddens perfectly dry litmus paper, according to Davy; according to Martens, it does not.

Calculation.			Dumas, Marchand.	H. Rose.	Bucholz.
2S	32·0	47·48	47·5	47·46	47·4
Cl	35·4	52·52	52·5	52·98	52·6
S^2Cl	67·4	100·00	100·0	100·44	100·0

	Vol.	Sp. gr.		Vol.	Sp. gr.
Vapour of sulphur	1	6·6556	=	½	2·2185
Chlorine gas	3	7·3629	=	1	2·4543
Vapour of dichloride of sulphur	3	14·0185	=	1	4·6728

(SCl = 201·17 + 221·33 = 422·50. (Berzelius.)

Decompositions.—1. Dichloride of sulphur, when put into water, sinks to the bottom in the form of oily drops, and on agitation, is very slowly decomposed, yielding hydrochloric acid, precipitated sulphur, and hyposulphurous acid—the last of which products gradually resolves itself into sulphurous acid and sulphur (Thomson):

$$2S^2Cl + 2HO = 2HCl + SO^2 + 3S.$$

A small quantity of sulphuric acid is however produced at the same time, even if the chloride still contains excess of sulphur. (Bucholz, H. Rose.) Since bichloride of sulphur (as obtained in combination with metallic chlorides) is resolved by water into hyposulphurous and sulphuric acid, it is possible that the dichloride may be a compound of the bichloride with 3 atoms of sulphur, S^3, SCl^2. (H. Rose.)—The liquid was found to contain undecomposed hyposulphurous acid, and consequently gave a black precipitate with nitrate of silver, even ten days after the decomposition by water. The separated sulphur amounts to 27·74 parts out of 100 parts of the dichloride, which is much less than three-fourths of the whole quantity of sulphur. (H. Rose.)—2. Phosphorus withdraws chlorine from sulphur, producing a rise of temperature of 40°, so that, on distilling the liquid, terchloride of phosphorus passes over, while sulphur remains behind. (Gaultier de Claubry, *Ann. Chim. Phys.* 7, 213.)—3. Hydrosulphuric acid resolves dichloride of sulphur into hydrochloric acid and sulphur. (H. Rose.)

$$S^2Cl + HS = 3S + HCl.$$

—4. Vapour of oil of vitriol and vapour of dichloride of sulphur passed through a red-hot tube yield sulphur, sulphurous acid, hydrosulphuric acid, hydrochloric acid, and chlorine. (Brault & Poggiale, *J. Pharm.* 21, 140.)—5. Dichloride of sulphur dissolves in ether when first mixed with it, but is afterwards decomposed, with slight evolution of heat. (Dumas.)

Combinations.—*a.* Dichloride of sulphur dissolves sulphur in large quantity; so much indeed when heated as to form a syrup, from which, on cooling, sulphur continues to separate for several weeks. When saturated with sulphur at ordinary temperatures, it has a clear yellow colour, and contains altogether 66·74 p. c. sulphur (H. Rose); consequently, about 4 At. sulphur to 1 At. chlorine. This solution has a specific gravity of 1·7, and when distilled, leaves the excess of sulphur behind; when the liquid evaporates gradually in the air, the sulphur which separates has a crystalline character. (Bucholz, Berthollet.)

b. Mixes easily with bisulphide of carbon. (A. Berthollet.)

c. Absorbs phosgene gas.

d. Combines with ammonia.

e. Combines with certain metallic chlorides. (H. Rose.)

b. Protochloride of Sulphur. SCl.

Einfach Chlorschwefel, Deutochlorure de Soufre.

Preparation.—1. Dry chlorine gas in large excess is passed for several days through flowers of sulphur; the liquid distilled between 60° and 70° (140°—158° F.); and the distillate, which still contains a little dichloride of sulphur, again distilled several times in a stream of chlorine gas, at a temperature below its boiling point. (Dumas; Soubeiran, *Ann. Chim. Phys.* 67, 74.) The chlorine is admitted during the distillation, through the tubulure of the retort. Even when chlorine gas is passed through sulphur for ten hours, the proportion of sulphur is not reduced below 37·51 per cent.; if a small portion be distilled from it, the distillate is found to contain 33·41 p. c.; a second portion, distilled below the boiling point, contains 32·55 p. c. of sulphur, and therefore approaches nearly to SCl. (H. Rose.) Dichloride of sulphur absorbs chlorine gas slowly, increasing considerably in volume by the absorption: when no more chlorine is absorbed, even after the passage of the gas has been continued for a long time, the liquid deposits Millon's solid protochloride of sulphur (*q. v.*) and at the same time evolves chlorine continuously. Its specific gravity is 1·625; it boils at 50° at first, evolving nearly pure chlorine; but afterwards, the boiling point rises to 64°; and then the liquid is found to contain 31·73 per cent. of sulphur. (Marchand.) If the liquid be distilled, after thrice repeated cohobation (I., 288) till it no longer evolves free chlorine, it is found to boil constantly at 78° (140·4° F.), and to contain 37·78 per cent. of sulphur; it is therefore a *$\frac{3}{4}$-chloride of sulphur*, S^4Cl^3. (Marchand.)

Properties. Dark, brown-red, thin liquid, of specific gravity 1·620; boils at 64° (147·2° F.); specific gravity of the vapour = 3·7. (Dumas.) Does not solidify at — 30°. (H. Rose.) Fumes and smells like the dichloride, but has more of the odour of chlorine than the latter; tastes sour, hot, and bitter. (Thomson.) According to Martens (*J. Chem. Med.* 13, 430), it reddens dry litmus paper fully; according to Davy, it does not.

	Calculation.		H. Davy.	Dumas. carlier.	Dumas. later.
S	16	31·13	30	30·36	31·9
Cl	35·4	68·87	67	69·64	68·1
S^2Cl	51·4	100·00	100	100·00	100·0

	Vol.	Sp. gr.		Vol.	Sp. gr.
Vapour of sulphur	1	6·6556	=	$\frac{1}{6}$	1·1093
Chlorine gas	6	14·7258	=	1	2·4543
Vapour of protochloride of sulphur	6	21·3814	=	1	3·5656

(SCl^2 = 201·17 + 2·221·33 = 643·83. Berzelius.)

Decompositions.—According to Dumas, protochloride of sulphur evaporates as a whole without decomposition; but, according to Marchand, it begins to boil at 50°, evolving nearly pure chlorine gas; afterwards tho boiling point rises to 64°. It also evolves chlorine when exposed to sunshine, and with sufficient force to break the vessel in which it is enclosed. —2. When a piece of potassium is dropt into about half a gramme of this liquid, a red light is often produced after about 40 seconds, and likewise an explosion which bursts the vessel. Vapour of protochloride of sulphur passed over red-hot iron or copper filings produces a chloride and

sulphide of the metal, with evolution of light and heat. (Dumas.)—3. In contact with water, protochloride of sulphur is slowly decomposed, the chief products being hydrochloric and hyposulphurous acid, which latter is further resolved into sulphurous acid and sulphur.

$$2SCl + 2HO = 2HCl + S^2O^2;$$

but, according to Rose, sulphuric acid is produced at the same time.—4. Nitric acid converts protochloride of sulphur, with violent effervescence, into hydrochloric and sulphuric acid. (Thomson.)—5. With aqueous ammonia, this substance forms sulphur, nitrogen gas, and sal-ammoniac. (Dumas.) Its relations with ammonia will be given under the heads of *Sulphide of Nitrogen* and *Nitrogen and Chlorine*.—6. Froths up violently with alcohol (Thomson); likewise with ether (Dumas).

Combinations.—*a*. It dissolves phosphorus, forming an amber-coloured solution. (Thomson.)

b. Absorbs phosgene gas.

c. Dissolves iodine, forming a deep-red liquid which does not conduct electricity. (Solly, *Pogg.* 37, 420.)

d. Combines with ammoniacal gas. (Soubeiran.)

e. Combines with chloride of arsenic. (H. Rose.)

Solid Protochloride of Sulphur. When chlorine gas is passed for a long time through liquid protochloride of sulphur, yellow crystals are produced, having the odour of the liquid protochloride. When exposed to the air, they evaporate quickly and completely in white fumes; dissolve readily in dichloride of sulphur, changing its yellow colour to brownish red; also in water, with loud hissing and slight deposition of sulphur. (Millon, *Compt. Rend.* 6, 207; also *J. pr. Chem.* 16, 57.) The same crystals were obtained by Marchand. They contain 30·93 per cent. of sulphur. When they dissolve in water, hydrochloric, sulphuric, sulphurous and hyposulphurous acids are produced, besides precipitated sulphur. Marchand regards them as pure protochloride of sulphur, and the liquid compound as containing a somewhat larger quantity of sulphur.

c. Bichloride of Sulphur.—Known only in combination with bichloride of titanium, bichloride of tin, or pentachloride of antimony. Resolved in contact with water, into sulphuric and hyposulphurous acid, the latter being subsequently converted into sulphurous acid, with deposition of sulphur. (H. Rose, *Pogg.* 42, 517.)

d. Terchloride of Sulphur.—May be obtained in combination with sulphuric acid.

B. Chlorosulphide of Phosphorus.

a. $PS^{10}Cl^2$, or $PS^6 + 2S^2Cl$.—When phosphuretted hydrogen gas is passed into dichloride of sulphur, this compound is formed together with hydrochloric acid.

$$5S^2Cl + PH^3 = PS^{10}Cl^2 + 3HCl.$$

Yellowish, very tenacious syrup.

Calculation.		
P	31·4	11·98
10S	160·0	61·02
2Cl	70·8	27·00
PS^{10}, Cl^2	262·2	100·00

Does not change under water, when first immersed, but afterwards becomes white on the surface and renders the water milky, from separation of sulphur; likewise imparts to it a powerful odour of hydrosulphuric acid, in consequence of the phosphorus absorbing oxygen from the water. The sulphur separated amounts to 44·43 per cent. It is rapidly oxidized by fuming nitric acid, with formation of sulphuric and phosphoric acids. (H. Rose.)

b. PS^2Cl^3 or PCl, 2SCl. Formed when dry hydrosulphuric acid gas is brought in contact with pentachloride of phosphorus,

$$PCl^5 + 2HS = PS^2\,Cl^3 + 2HCl.$$

The hydrosulphuric acid gas is either slowly passed over the chloride of phosphorus contained in a glass bulb; or the latter is poured into a vessel full of the gas. The same compound is obtained if an excess of hydrosulphuric acid is employed. 100 parts of pentachloride of phosphorus yield 81·775 parts of the new compound. It is purified by distillation in a small retort.

Opalescent at first; afterwards becomes colourless and transparent; heavier than water. Boils at 125°; and fumes slightly in the air. Has a characteristic odour, somewhat pungent and aromatic, and likewise smells of hydrosulphuric acid (formed by the decomposing action of the moisture in the air).

	Calculation.	
P	31·4	18·51
2S	32·0	18·87
3Cl	106·2	62·62
PS^2Cl^3	169·6	100·00

Water decomposes it, in the course of a few days; more rapidly when the mixture is agitated; with the aid of heat, the decomposition is complete in a few hours: the products are hydrochloric, hydrosulphuric, and phosphoric acids.

$$PS^2Cl^3 + 5HO = PO^5 + 2HS + 3HCl.$$

The water, however, is rendered milky, from separation of a small quantity of free sulphur. Aqueous ammonia or potash causes a similar decomposition, but much more rapidly. (Serullas.)

The oil, especially when warmed, dissolves a small excess of phosphorus or sulphur, which again separates for the most part on cooling, and remains behind when the oil is distilled. (Serullas, *Ann. Chim. Phys.* 42, 25; also *Pogg.* 17, 165; also *Schw.* 57, 366; also *N. Tr.* 21, 1, 214.)

Burning sulphide of carbon is extinguished in chlorine gas; at ordinary temperatures, that liquid absorbs a small quantity only of the gas; which is again expelled on heating the liquid. (Berzelius.)

¶ C. Chlorosulphide of Carbon. CSCl.

Formation and Preparation.—1. When a few grammes of bisulphide of carbon are introduced into a flask filled with perfectly dry chlorine gas, the flask, carefully closed, and left for a few days either in the dark or in sun-light, the colour of the chlorine gradually disappears, and the sulphide of carbon is converted into a liquid of a deep yellow colour. On opening the flask, the gas within is found to be rarefied. The liquid thus formed is a mixture of protochloride of sulphur with the compound under consideration:

$$CS^2 + 2Cl = SCl + CSCl.$$

By digestion in water, the chloride of sulphur is decomposed and the chlorosulphide of carbon separates in the form of an oily liquid. To purify it from the acid products formed by the decomposition of the chloride of sulphur, it must be several times distilled with water and a small quantity of magnesia.—In preparing this compound, it is essential that the materials be perfectly free from moisture; for if water is present, another compound of chlorine, sulphur, and carbon, is produced, which will be described immediately. (*See next page.*)—2. By passing a mixture of hydrosulphuric acid gas and vapour of perchloride of carbon, C^2Cl^4, through a tube kept at a moderate red-heat; hydrochloric acid is formed at the same time (Kolbe):

$$C\,Cl^2 + HS = HCl + CSCl.$$

Properties. Yellow liquid, not miscible with water; has a very peculiar and powerful odour; irritates the eyes very strongly. Specific gravity $=1\cdot46$. Boiling point 70° (158° F.); these numbers probably require correction, as it is difficult to obtain the compound quite free from bisulphide of carbon. (Kolbe).

		Calculation. *a.*	*b.*	Kolbe.
C	6	10·45	9·62	10·72
S	16	27·87	25·66	32·16
Cl	35·4	61·67	56·76	56·76
CSCl	57·4	100·00	92·04	99·64

It will be observed that the experimental and calculated numbers differ considerably. Kolbe attributes this difference to the presence of undecomposed bisulphide of carbon; indeed, it appears from calculation *b*, in which the quantity of chlorine is made equal to that determined by the analysis, that the excess of carbon (1·1), and that of sulphur (6·5), are very nearly in the proportion in which those elements exist in bisulphide of carbon. Admitting the correctness of the formula CSCl—which accords both with the mode of formation of the substance, and also with its reactions—it will be seen that the chlorosulphide of carbon is the analogue of phosgene, COCl, the atom of oxygen being replaced by an atom of sulphur. It may also be regarded as $C^2Cl^4, 2CS^2$. that is to say, as a compound of 2 atoms of bisulphide of carbon with 1 atom of Regnault's perchloride of carbon, just as phosgene may be regarded as $C^2Cl^4, 2CO^2$ (*vid.* p. 326). This view of its constitution is also rendered probable by its mode of formation. For, when vapour of bisulphide of carbon and dry chlorine gas are brought together at a red heat, the products are perchloride of carbon and free sulphur; so that, if the second view of the composition of the chlorosulphide be admitted, it will follow, that the action of chlorine on bisulphide of carbon at ordinary temperatures, differs from that which takes place at high temperatures, only in this respect—that, in the former case, the perchloride of carbon produced, enters into combination with a portion of the undecomposed sulphide of carbon, while in the latter, it does not. (Kolbe.)

Decompositions. Chlorosulphide of carbon is not decomposed by water or by acids, not even by fuming nitric acid. Caustic potash decomposes it slowly, the products being carbonate of potash, sulphide of potassium, and perchloride of carbon: thus, (halving all the numbers),

$$2CSCl + 3KO = KO, CO^2 + 2KS + CCl^2$$
$$\text{or: } CCl^2, CS^2 + 3KO = CCl^2 + KO, CO^2 + 2KS.$$

This decomposition is in favour of the second view of the constitution of the substance. (Kolbe, *Ann. Pharm.* 45, 53.) ¶

D. Carbonate of Bichloride of Sulphur. $CSCl^2O^2$.

Chlor-hyposulphite of Chloro-carbonic oxide, Chlorunterschwefligsaures Chlorkohlenoxyd (Berzelius); *Oxychloride of Sulphide of Carbon, Sauerstoff-chlorschwefelkohlenstoff;—Sulphite of Perchloride of Carbon, Schwefligsaures Kohlensuperchlorid* (Kolbe).

Formation and Preparation.—1. One part of bisulphide of carbon is digested for a long time with 16 parts of a mixture of fuming nitric and concentrated hydrochloric acid, the materials being put into an imperfectly closed vessel, and kept at a temperature of 21°. (70° F.) The odour of chloride of sulphur becomes perceptible—the sulphide of carbon acquires an orange-yellow colour—then becomes paler and more tenacious—nitrous fumes are evolved—and, in the course of three months, the whole becomes converted into a solid mass, which may be freed from adhering acid by washing with cold water. (Berzelius and Marcet.)—2. This substance is more quickly formed by exposing bisulphide of carbon to the action of moist chlorine gas. (Berzelius.) ¶. A capacious glass bottle, holding about 3 pints and fitted with a ground stopper, is half filled with a mixture of peroxide of manganese and hydrochloric acid; about 800 grains of bisulphide of carbon are then added, and the vessel quickly closed. The mixture is first placed for some days in a cool place, and afterwards exposed, for several days longer, to a temperature of 30° (86° F.), and frequently shaken, till the greater part of the bisulphide of carbon is converted into the new compound; in summer, it is best to expose the mixture to the direct rays of the sun. The action may be greatly accelerated by adding from 6 to 10 oz. of ordinary commercial nitric acid to the mixture. There is no danger of the vessel bursting from internal pressure, provided the precaution be taken of raising the stopper from time to time. The whole contents of the bottle are subsequently turned out into a large flask, and distilled in an oil-bath, the volatile products being condensed by means of a Liebig's condenser, having a wide tube not turned down at the lower end. The first portions of the distillate consist of undecomposed bisulphide of carbon, mixed with another liquid of yellow colour and offensive odour: little or no free chlorine escapes. Afterwards, the carbonate of bichloride of sulphur distils over, and solidifies in the condensing tube; when the distillation is over, it may be easily separated by a gentle thrust. The weight of the product is more than double that of the bisulphide of carbon employed. The action is as follows:

$$CS^2 + Cl^4 + 2HO = SCl^2, CO^2 + 2HCl + S$$

(Kolbe, *Ann. Pharm*, 54, 148.)¶.

Properties. Colourless, transparent, crystalline mass, (apparently cubical), resembling camphor. ¶. It closely resembles camphor in external appearance, and, like that substance, sublimes when heated in close vessels, condensing on the side in small, colourless, transparent, rhombic tables, having a diamond lustre. The smaller angle of the base is so near 60°, that, if the opposite acute lateral edges be replaced by planes, an almost regular six-sided prism will be formed. Both forms are obtained, very well developed, by slowly subliming the substance by the warmth of the hand, in a glass tube exhausted of air and hermetically sealed. The six-sided prisms collect on the part nearest to the hand; the rhombic prisms at the further end. The crystals when moist, are white and

opaque, and form arborescent ramifications without definite crystalline form, like frost on windows. (Kolbe.) ¶.

This substance fuses at a gentle heat, and crystallizes again on cooling; at a somewhat higher temperature, it sublimes without residue. (Berzelius). Begins to melt at 135° (275° F.), boils at 170° (338° F.), and may be distilled, either alone or with water. (Kolbe.) Odour, sharp and disagreeable, resembling that of chloride of sulphur; taste, sharp, burning, and afterwards acid. (Berzelius.) Its odour is so pungent and peculiar, that it may always be detected by that character, even in the smallest quantities; it excites a rapid flow of tears, and when inhaled in rather large quantities, produces an intolerable irritation in the throat, but without otherwise injuring the health. (Kolbe.) Does not redden litmus paper when dry, barely when moist. (Berzelius.) Moist litmus paper is instantly reddened by it, in consequence of partial decomposition. (Kolbe.) Specific gravity of the vapour = 7·43. (Kolbe.)

	Calculation.		Kolbe.	Berzelius and Marcet.	
C	6·0	5·5	5·4	Carbonic acid	21·63
S	16·0	14·7	14·9	Sulphurous acid	29·63
2Cl	70·8	65·1	65·1	Anhydrous muriatic acid (hyp.)	48·74
2O	16·0	14·7	14·6		
$CSCl^2O^2$	108·8	100·0	100·0		100·00

(Kolbe.)	Vol.	Sp. gr.
Vapour of perchloride of carbon CCl^2	1	5·29
Sulphurous acid gas, SO^2	1	2·22
Vapour of sulphite of perchloride of carbon	1	7·51

($COCl^2$, + SO + 2Cl = 619·10 + 301·17 + 442·66 = 1362·93. Berzelius.)

This compound may be regarded as carbonate of bichloride of sulphur, $= SCl^2, CO^2$; or, with Berzelius, as a compound of phosgene and hyposulphurous acid, with which one atom of chlorine is united, $= COCl + SOCl$; or, with Kolbe, as sulphite of bichloride of carbon, $= CCl^2, SO^2$.

Decompositions.—1. By water, especially at a boiling heat, this compound is gradually resolved into carbonic, sulphurous, and hydrochloric acid; the same effect is produced, but more quickly, by caustic potash.

$$CSCl^2O^2 + 2HO = CO^2 + SO^2 + 2HCl.$$

2. By red-hot iron filings, into chloride of iron, sulphide of iron, carbonic acid, and carbonic oxide.

¶ 3. When it is heated with a large excess of concentrated oil of vitriol, the products are sulphurous acid, hydrochloric acid, and phosgene gases:

$$2(CCl^2, SO^2) + 2(HO, SO^3) = CCl^2, CO^2 + 2HCl + 4SO^2.$$

—4. It bears a moderately high temperature without alteration; but when passed through a glass tube kept a dull red heat, it is resolved into protochloride of carbon, sulphurous acid, and free chlorine, the former distilling over in the liquid form, the two latter escaping as gas. (Kolbe.) ¶. [For other modes of decomposition *see* the next page.]

Combinations.—*a.* Soluble in bisulphide of carbon.—*b.* With ammonia.—*c.* With alcohol, ether, volatile oils, and fixed oils. (Berzelius & Marcet, *Schw.* 9, 298; also *Gilb.* 48, 161.—Kolbe, *Ann. Pharm.* 54. 148.)

¶. E. CARBONATE OF PROTOCHLORIDE OF SULPHUR. $CSClO^2$

Sulphite of Protochloride of Carbon, Schwefligsaures Kohlenchlorid.

Formation. By the action of sulphurous acid on the carbonate of bichloride of sulphur, in contact with water or the elements of water, sulphuric and hydrochloric acid being formed at the same time.

$$CSCl^2O^2 + SO^2 + HO = CSClO^2 + SO^3 + HCl.$$

2. By the action of sulphuretted hydrogen on an alcoholic solution of $CSCl^2O^2$, hydrochloric being also formed and sulphur precipitated:

$$CSCl^2O^2 + HS = CSClO^2 + HCl + S.$$

3. Protochloride of tin dissolves carbonate of bichloride of sulphur in large quantity, with great evolution of heat, the products being bichloride of tin and carbonate of protochloride of sulphur.

$$CSCl^2O^2 + SnCl = CSClO^2 + SnCl^2.$$

4. By the action of nascent hydrogen on the carbonate of bichloride of sulphur, *e.g.* when iron or zinc is digested in an acidulated solution of that compound in alcohol, diluted as much as possible without causing precipitation; also when the same solution is decomposed by the electric current.

This compound has not been obtained in the separate state, and it does not combine with salifiable bases: hence its composition cannot be determined by actual analysis, but its mode of formation and its reactions with other bodies show that it differs from the preceding compound, only in containing one atom less of chlorine.

Calculation.		
C	6	8·17
S	16	21·80
Cl	35·4	48·23
2O	16	21·80
$CSClO^2$	73·4	100·00

It may be regarded either as carbonate of protochloride of sulphur, SCl,CO^2, (in accordance with Gmelin's view of the preceding compound), or, with Kolbe, as a sulphite of protochloride of carbon, CCl,SO^2.

This compound is soluble in water and in alcohol; it is obtained in the state of solution, by passing a stream of sulphurous acid gas through an alcoholic solution of the sulphite of perchloride of carbon. After a certain quantity of the gas has been passed through, the liquid becomes miscible with water without decomposition: it then contains, besides free sulphurous acid, which is easily expelled by heat, hydrochloric acid, sulphuric acid, and the sulphite of protochloride of carbon. The same results are obtained, though more slowly, by digesting the sulphite of perchloride of carbon in aqueous solution of sulphurous acid.

The solution in water or alcohol is colourless and inodorous; cannot be concentrated by evaporation in open vessels; has an acid reaction [arising from the presence of sulphuric or hydrochloric acid ?], but shows no tendency to combine with salifiable bases. It has a strong attraction for oxygen, and when exposed to the air, is partially converted into phosgene gas and sulphuric acid:

$$CSClO^2 + 2O = COCl + SO^3.$$

A small quantity of the aqueous solution spread out upon a plane surface

so as to expose as large a surface as possible to the air, will fill a closed room with the suffocating fumes of phosgene and sulphurous acid to such a degree, as to render the air almost irrespirable.

Chlorine gas passed through the aqueous solution produces a copious white precipitate, arising from the reproduction of sulphite of perchloride of carbon, which is insoluble in water:

$$CSClO^2 + Cl = CSCl^2O^2.$$

Bromine produces a similar precipitate, consisting of a compound containing both chlorine and bromine, which has not been further investigated. Iodine causes no precipitation.

By the action of various reagents on the two compounds just described, Kolbe has formed a series of acids containing the elements of hyposulphuric acid, and of certain organic radicals, as formyl, elayl, methyl, &c. As far as their mode of formation is concerned, these compounds are strictly inorganic; but in their composition and reactions, they bear so close a resemblance to certain organic compounds that the consideration of them is best referred to the department of Organic Chemistry (especially as all the hydrocarbons and the chloride of olefiant gas are referred by the author to that part of the work: *vid.* p. 326). A brief sketch of them may however be introduced in this place.

a. Chlorocarb-hyposulphuric acid, (*Chlorkohlenunterschwefelsäure*): $HO, C^2Cl^3S^2O^5$.—Formed by the action of caustic potash at a gentle heat on sulphite of perchloride of carbon.

$$2(CCl^2, SO^2) + 2KO = KO, C^2Cl^3S^2O^5 + KCl.$$

The hydrate of this acid crystallizes in small deliquescent prisms; it may be partially sublimed without decomposition. It is not oxidized by fuming nitric acid or aqua-regia, and has so powerful an affinity for bases that it even expels hydrochloric acid from its compounds. Its salts are all soluble in water and alcohol, and crystallize with facility. When heated, they are resolved into phosgene gas, sulphurous acid, and metallic chloride.

$$KO, C^2Cl^3S^2O^5 = CCl^2, CO^2 + 2SO^2 + KCl.$$

b. Chlorformyl-hyposulphuric acid: $HO, C^2HCl^2S^2O^5$.—Formed by the action of caustic alkalis on sulphite of protochloride of carbon, the elements of water taking part in the reaction,

$$2(CCl, SO^2) + KO + HO = KO, C^2HCl^2S^2O^5;$$

also by the action of metallic zinc on the compound *a*, chloride of zinc being formed at the same time,

$$HO, C^2Cl^3S^2O^5 + 2Zn = ZnO, C^2HCl^2S^2O^5 + ZnCl.$$

Resembles the preceding compound in most of its properties. Its salts, when heated, give off phosgene gas, sulphurous acid, and water, and leave a residue consisting of charcoal and metallic chloride.

c. Chlorelayl-hyposulphuric acid: $HO, C^2H^2ClS^2O^5$.—Formed by the continued action of nascent hydrogen on chlorformyl-hyposulphuric acid:

$$HO, C^2HCl^2S^2O^5 + 2H = HO, C^2H^2ClS^2O^5 + HCl.$$

When zinc is immersed in an aqueous solution of chlorformyl-hyposulphuric acid, it dissolves, with evolution of hydrogen; and the hydrogen, as it is set free, converts a portion of the acid into chlorelayl-hyposul-

phuric acid. But complete transformation can only be attained by subjecting an acidulated solution of a salt of acid *a* or *b* to the action of the galvanic current.—The hydrate of this acid is a viscid, strongly acid liquid, which bears a heat of 140° C. without decomposition; at —16·6° C. it assumes a syrupy consistence; in other respects, it resembles the compound *a*. All its salts are soluble in water, and most of them crystallizable.

d. Methyl-hyposulphuric acid: $HO, C^2H^3S^2O^5$.—This acid, which differs from the rest of the series in not containing chlorine, is formed when a *neutral* solution of chlorocarb-hyposulphate of potash is decomposed by the electric current, the electrodes being formed of amalgamated zinc plates:

$$KO, C^2Cl^3S^2O^5 + 6Zn + 6HO = KO, C^2H^3S^2O^5 + 6ZnO + 3HCl.$$

Also when amalgam of potassium is immersed in the same solution:

$$KO, C^2Cl^3S^2O^5 + 6K + 3HO = KO, C^2H^3S^2O^5 + 3KCl + 3KO.$$

In both cases, the immediate agent in the conversion is nascent hydrogen: no hydrogen is evolved till the transformation is complete.—The concentrated solution of this acid is a sour, inodorous, viscid liquid, which may be heated to nearly 130° C. without decomposition: at that temperature, it begins to turn brown from commencing decomposition. Does not crystallize when pure. In stability and affinity for salifiable bases, it is not inferior to chlorocarb-hyposulphuric acid. Its salts are soluble and crystallizable. (Kolbe. *Beiträge zür Kenntniss der gepaarten Verbindungen, Ann. Pharm.* 49, 339; 54, 143.) ¶

F. Sulphate of Hydrochloric Acid.—Anhydrous sulphuric acid absorbs a very large quantity of hydrochloric acid, being thereby converted into a transparent and colourless liquid.—Oil of vitriol does not absorb hydrochloric acid gas. (Aimé, *J. Pharm,* 21, 88; also *J. pr. Chem.* 6, 79.)

G. Sulphate of Pentachloride of Phosphorus?—Vapour of anhydrous sulphuric acid is passed in excess over terchloride of phosphorus contained in a receiver surrounded with ice, the liquid decanted from the excess of acid which has solidified in the receiver, and then distilled. Sulphurous acid is evolved (inasmuch as part of the phosphorus is converted into phosphoric acid, and the terchloride of phosphorus thereby converted into pentachloride). Between 40° and 50°, which range of temperature is maintained for a day, another portion of superabundant acid passes over and condenses in the ice-cold receiver; afterwards, at a somewhat higher temperature, a mixture of sulphuric acid and the new compound distils over, and solidifies after some time: finally—the receiver having been changed—there passes over a liquid which does not solidify at any temperature. Nevertheless, its boiling point is not constant, and it undergoes more or less alteration every time it is distilled. It begins to boil at 137°; then the boiling point rises to 160°—165°; and in the retort there remains a syrup which dissolves in water with great evolution of heat, producing sulphuric, hydrochloric, and phosphoric acid; when more strongly heated, it leaves a gummy residue of metaphosphoric acid.

The compound when purified by distillation, is of an oily consistence. When poured into water, it sinks to the bottom in drops, which slowly dissolve, yielding hydrochloric, sulphuric, and ordinary phosphoric acid.

The oil may be regarded as a compound of sulphuric acid and pentachloride of phosphorus, often mixed with pentasulphate of terchloride of sulphur; or as a loose and variously constituted compound of pentasulphate of chloride of sulphur with phosphate of pentachloride of phosphorus. (H. Rose gives the preference to the latter view.) Different portions of the liquid prepared at different times, or collected at different stages of the distillation, were found to contain, in 100 parts, the following quantities of sulphur and chlorine:

	a	*b*	*c*	*d*	*e*
S	21·90	11·47	7·51	11·84	13·59
Cl	38·41	49·51	58·91	52·09	51·36

d and *e* were obtained by a second rectification; moreover, *d* was the second, and *e* was the third part of the distillate. (H. Rose, *Pogg.* 44, 304.)

H. Sulphate of Terchloride of Sulphur.

a. Bisulphate of Terchloride of Sulphur. $SCl^3, 2SO^3$

Chlorosulphuric acid, Chlorschwefelsäure, Acide chlorosulfurique.

A mixture of sulphurous acid and chlorine gases in equal volumes, exposed to sunshine in the month of June, produces fumes in the course of a few hours; and after some days, condenses, for the most part, to a liquid. This liquid may be purified by distillation over mercury, the receiver being changed after a while, because the first portions of the distillate contain sulphurous acid. (Regnault.)

Colourless liquid, of specific gravity 1·659, at 20° (68° F.); boils at 77, (170·6° F.); specific gravity of the vapour, 4·665. (Regnault.)

Calculation, according to Regnault.				Or.		
S	1	16·0	23·74	SO^2	32·0	47·48
O	2	16·0	23·74	Cl	35·4	52·52
Cl	1	35·4	52·52			
$SClO^2$	1	67·4	100·00	SO^2, Cl	67·4	100·0

	Vol.	Sp. gr.
Sulphurous acid gas	1	2·2186
Chlorine gas	1	2·4543
Vapour	1	4·6729

May be regarded as sulphurous acid, in which 1 At. O is replaced by 1 At. Cl, or as a compound of sulphurous acid with chlorine, or as a compound of terchloride of sulphur with sulphuric acid: $3(SClO^2) = SCl^3 + 2SO^3$.

Water converts it, with great evolution of heat, into hydrochloric and sulphuric acid.

$$SO^2Cl + HO = SO^3 + HCl.$$

It does not combine with salifiable bases, and therefore, perhaps, scarcely deserves to be called an acid. (Regnault.)

The following process yields this compound, mixed with about an equal quantity of oil of olefiant gas. A mixture of sulphurous acid and olefiant gases evolved by heating 1 part of absolute alcohol with 6 parts of oil of vitriol, is passed through two bottles filled with oil of vitriol, by which ether vapour and aqueous vapour are absorbed, and then mixed in a glass globe with dry chlorine gas. The two gases condense

into a liquid, of pungent, suffocating odour. It may be freed from adhering sulphurous acid and chlorine by distillation; but the receiver must be changed after a while, because the sulphurous acid and chlorine pass over first. From oil of olefiant gas, however, it cannot be entirely freed; because the boiling points of that liquid and of chlorosulphuric acid are nearly equal.

The compound obtained by this process contains from 29 to 51 per cent. of oil of olefiant gas, and 71—49 of chlorosulphuric acid.

In water, chlorosulphuric acid is converted—with separation of the oil and great development of heat—into sulphuric and hydrochloric acid; the same effect is produced, but more rapidly, by potash. On the other hand, the liquid may be distilled over burnt lime or baryta without decomposition. In contact with ammoniacal gas, the chlorosulphuric acid contained in it is converted into sal-ammoniac and sulphamide ($SO^2Cl + 2NH^3 = NH^3, HCl + NH^2SO^2$.) (*Regnault*).

b. Pentasulphate of Terchloride of Sulphur, $SCl^3, 5SO^3$.

Preparation. Dichloride of sulphur surrounded with a freezing mixture rapidly absorbs the vapour of anhydrous sulphuric acid, thereby acquiring a brown colour; but if afterwards kept for 24 hours in a close vessel, at 0°, it regains its yellow colour, provided the sulphuric acid is not in excess. At temperatures below 0°, no sulphurous acid escapes; but a few degrees above 0°, that gas is rapidly evolved, sometimes bursting the containing vessel. When heated in a retort, the liquid soon boils, with violent evolution of sulphurous acid; and, if the sulphuric acid is not in excess, the evolution of sulphurous acid continues for a while, as the temperature gradually rises; then, between 30° and 40°, chloride of sulphur passes over; then a mixture of the latter with pentasulphate of terchloride of sulphur; and lastly, at 145°, the pentasulphate in a state of purity. The free chloride of sulphur mixed with the pentasulphate may be removed by rectification.

$$3S^2Cl + 15SO^3 = SCl^3, 5SO^3 + 15SO^2.$$

When anhydrous sulphuric acid is passed in large excess through dichloride of sulphur, a thin blue liquid is obtained—or a solid if the acid is in very great excess—which, when heated, becomes colourless, evolves sulphurous acid, and is converted into a mixture of pentasulphate of terchloride of sulphur and excess of sulphuric acid. On heating this liquid still further, sulphuric acid passes over first, then a mixture of that acid with pentasulphate of terchloride of sulphur, and finally the latter alone. The blue colour is due to the combination of the anhydrous sulphuric acid with a portion of the sulphur contained in the dichloride. —2. From 20 to 30 volumes of good fuming oil of vitriol are mixed with one volume of chloride of sulphur saturated as much as possible with chlorine; and the dark brown mixture, on the surface of which a lighter coloured liquid generally floats, is subjected to distillation. The excess of chloride of sulphur passes over first, together with a large quantity of sulphurous acid; afterwards the sulphuric acid compound, which should be collected in a separate receiver; common oil of vitriol remains in the retort. The liquid is distilled till the residue no longer precipitates a silver solution, and the distillate freed by rectification from oil of vitriol which may have passed over with it in the previous distillations. (H. Rose.)

Colourless, oily liquid, specific gravity = 1·818, at 16° (60·8° F.), boils at 145° (293° F.); distils without residue. Specific gravity of the vapour, 4·481. Fumes strongly in the air, but less strongly than anhydrous sulphuric acid; has a peculiar odour, quite distinct from that of sulphurous acid. (H. Rose.)

		Calculation.		H. Rose.
6S	....	96·0	29·80	30·35
15O	....	120·0	37·24	38·15
3Cl	....	106·2	32·96	31·50
$S^6O^{15}Cl^3$	....	322·2	100·00	100·00

	Vol.	Sp. gr.		Vol.	Sp. gr.
Sulphuric acid vapour	2	13·3112	=	$\frac{1}{5}$	1·3311
Oxygen gas	15	16·6395	=	$1\frac{1}{2}$	1·6639
Chlorine gas	6	14·7258	=	$\frac{3}{5}$	1.4726
Vapour	10	44·6765	=	1	4·4676

May be regarded as 2 At. sulphuric acid in which 1 At. O is replaced by 1 At. Cl, = S^2O^5Cl.

Decompositions. The vapour of this compound withstands a temperature of 217° (423° F.) without decomposition; but when passed through a red-hot tube, it is partly resolved into sulphurous and sulphuric acid, the quantity decomposed increasing as the tube is more strongly ignited—so that, as the process goes on, the portion which remains undecomposed becomes mixed with a continually increasing quantity of free sulphuric acid. [The decomposition probably takes place in this manner: $S^6O^{15}Cl^3 = 3SO^3 + 3SO^2 + 3Cl$]. When the tube is at a dull red heat, the distillate contains about $SCl^3 + 7SO^3$; at a stronger heat, $SCl^3 + 11SO^3$; at a still higher temperature, the quantity of sulphuric acid becomes so great, that a portion of it crystallizes out.—2. Under water, the compound is slowly resolved into sulphuric and hydrochloric acid.

$$S^2O^5Cl + HO = 2SO^3 + HCl.$$

When put into water, it first sinks to the bottom in oily drops, and does not dissolve for several hours, even when stirred. It appears to be converted into a hydrate before it dissolves. If it contains free chloride of sulphur, it deposits sulphur when decomposed by water, and emits a faint odour of sulphurous acid.—3. When this compound is mixed with common salt, great heat is evolved, and a solid, translucent mass is formed, which no longer fumes on exposure to the air. When this mass is subjected to distillation, part of the pentasulphate passes over undecomposed, but mixed with free chlorine; the remaining portion, together with the salt, is converted into chlorine, sulphurous acid, and bisulphate of soda. (H. Rose.) Probably in this manner:

$$NaCl + S^6O^{15}Cl^5 = NaO,2SO^3 + 4SO^2 + 4Cl.$$

Combinations. *a.* Miscible with excess of anhydrous sulphuric acid, which, however, passes over first when the mixture is distilled—and is therefore but loosely combined.

b. Absorbs chlorine gas and forms a yellowish green liquid, which smells strongly of chlorine—evolves that gas with effervescence, even at 25°—appears to boil at 112°—and becomes colourless again after the chlorine has escaped.

c. With ammonia: *vid. Nitrogen and Chlorine.*

¶ I. SULPHATE OF BICHLORIDE OF SULPHUR. SCl^2, SO^3.

Discovered by Millon: formed by the action of moist chlorine gas on sulphur, or chloride of sulphur.—Large, transparent, colourless crystals, which are decomposed by alcohol or water, or even by exposure to damp air. When heated in a tube, they fuse, and are converted into a very mobile liquid, which is isomeric with them. This liquid, when digested in water, undergoes slow decomposition, the products being sulphuric, sulphurous, and hydrochloric acids:

$$SCl^2, SO^3 + 2HO = SO^3 + SO^2 + 2HCl.$$

(Millon. *J. Pharm.* 6, 413; abstr. *Ann. Pharm.* 52, 230.) ¶.

CHLORINE AND SELENIUM.

A. CHLORIDE OF SELENIUM.

Selenium, when chlorine gas is passed over it, melts at first, with disengagement of heat, to a brown liquid, which is afterwards converted by a larger quantity of chlorine into a white solid mass; on adding selenium to this substance as long as it is dissolved, the white mass is again converted into a brown liquid.

a. *Dichloride of Selenium.*

Transparent, brownish yellow oil, heavier than water; volatile. —Slowly decomposed by water into hydrochloric acid, selenious acid, and selenium, which long retains a small quantity of chlorine, and with it an oily consistence. (Berzelius.)

$$2Se^2Cl + 2HO = SeO^2 + 3Se + 2HCl.$$

Calculation, according to Berzelius.

2Se	80·0	69·3
Cl	35·4	30·7
Se^2Cl	115·4	100·0

b. *Bichloride of Selenium.*

White solid mass, which volatilizes in yellow vapours more readily than *a*; does not fuse before volatilizing, but merely contracts, and deposits itself on colder substances in small white crystals. These, when again sublimed, unite into a dense mass which cracks on cooling. With water it forms, with rise of temperature and slight effervescence, a colourless and transparent solution of hydrochloric and selenious acids.

$$SeCl^2 + 2HO = SeO^2 + 2HCl.$$

(Berzelius, *Ann. Chim. Phys.* 9, 225.)—When a seleniate is heated with common salt and oil of vitriol, no terchloride of selenium is obtained; but bichloride of selenium mixed with free chlorine passes over first, and then an oily mixture of selenious acid and sulphuric acid in green vapours. (H. Rose, *Pogg.* 27, 575.)

Calculation, according to Berzelius.

Se	40·0	36·1
2Cl	70·8	63·9
$SeCl^2$	110·8	100·0

B. Sulphate of Chloride of Selenium?

Bichloride of selenium absorbs the vapour of anhydrous sulphuric acid but slightly at ordinary temperatures; but if the vessel containing the two substances is closely corked and placed in a warm room, the two bodies slowly unite, without disengagement either of sulphurous acid or of chlorine, and form a very dense, greenish yellow syrup; the excess of sulphuric acid remains in a crystalline form. On distilling the syrup at a gentle heat, the excess of sulphuric acid passes over first; the residue in the retort solidifies, on cooling, to a white crystalline mass. This, when more strongly heated, melts to a light brown liquid and evolves—with disengagement of chlorine, but not of sulphurous acid—a reddish yellow vapour resembling hyponitric acid, which condenses to a colourless syrup, and finally to a white mass resembling wax. The latter substance is freed from adhering chlorine by a second distillation. After this treatment, it boils constantly at 187°, and may be redistilled without leaving any residue or undergoing further decomposition.—It contains on the average 12·895 per cent. of sulphur and 36·885 of chlorine; and, according to H. Rose, may be regarded as: $2\ (SeCl^3, 5SO^3) + 5\ (SeCl^2, SeO^2)$. It deliquesces rapidly in the air, exhaling the odour of hydrochloric acid, and dissolves readily in water, without first sinking to the bottom in oily drops; the solution, which is generally coloured red, from the presence of a small quantity of free selenium, contains hydrochloric, sulphuric, and selenious acid (no selenic acid). (H. Rose, *Pogg.* 44, 315. [If the compound is regarded as: $2\ (Se^2Cl^3) + 5SO^3$, the percentage will be: 28·96 Se, 34·83 Cl, 14·48 S, and 21·72 O.]

Chlorine and Iodine.

A. Chloride of Iodine.

Dry iodine rapidly absorbs chlorine gas, the temperature rising to 100°; when the iodine is in excess, the resulting compound is reddish-brown and fluid; but when the chlorine predominates, it is yellow and solid. (Gay-Lussac.)

a. Protochloride of Iodine.

Preparation.—1. By passing dry chlorine gas over dry iodine till the latter is converted into a perfectly fluid compound, but no longer.—2. By distilling 1 part of iodine with 4 parts of chlorate of potash. In this case, oxygen gas is disengaged and a mixture of iodate and perchlorate of potash remains in the retort. (Berzelius, *Lehrb.* 1, 261.) Since this distillate, according to Berzelius, is yellow or reddish coloured, and is also capable of taking up an additional quantity of iodine, a question arises whether it may not contain somewhat more than one atom of chlorine.

Properties. Reddish-brown, oily liqnid (Gay-Lussac), having a penetrating odour of chlorine and iodine (Gay-Lussac); attacks the eyes strongly (Kane); tastes slightly acid, powerfully astringent, and biting. (Berzelius.) Stains the skin deep yellow and produces smarting. (Kane.)

Decolorizes solution of indigo (Gay-Lussac) and litmus; does not give a blue colour with starch. (D. Vogel.)

	Calculation.		Kane.		Vol.
I	126·0	78·07	76·94	Vapour of Iodine	1
Cl	35·4	21·93	23·06	Chlorine gas	1
ICl	161·4	100·00	100·00		

Decompositions.—1. This compound, when heated, gives off terchloride of iodine, whilst pure iodine remains behind. A concentrated aqueous solution may likewise be resolved by repeated distillation into terchloride of iodine, which passes over, and a residue of iodine. (Kane.)—2. An aqueous solution of sulphurous or of hydrosulphuric acid blackens protochloride of iodine by separating iodine from it. (A. Vogel, *Kastn. Arch.* 10, 119.)—3. A concentrated solution, treated with red or brown peroxide of lead, oxide of copper, or red oxide of mercury, yields a metallic chloride and iodide, with separation of a small quantity of iodine and considerable evolution of oxygen gas. (Kane.)—4. With aqueous solutions of the fixed alkalis, protochloride of iodine yields metallic chloride, alkaline iodate, and free iodine; and the iodine dissolves in excess of the alkali, yielding iodide and iodate. (Gay-Lussac.)

$$6KO + 5ICl = 5KCl + KO, IO^5 + 4I.$$

—5. With aqueous ammonia, it yields hydrochlorate of ammonia and a precipitate of iodide of nitrogen. (Mitscherlich.)

$$3ICl + 4NH^3 = 3(NH^3,HCl) + NI^3.$$

—6. From a concentrated solution of protochloride of iodine, a strong solution of corrosive sublimate throws down iodide of mercury, leaving terchloride of iodine in solution. (Kane.)

$$2ICl + HgCl = HgI + ICl^3.$$

From a concentrated aqueous solution of this compound, a small quantity of an aqueous solution of protochloride of tin separates iodine; on the addition of a larger quantity of the chloride of tin, however, the iodine disappears, and brilliant orange-coloured needles of prot-iodide of tin make their appearance. First:

$$ICl + SnCl = I + SnCl^2;$$

Afterwards, with 2 atoms more of chloride of tin:

$$ICl + 3SnCl = SnI + 2SnCl^2. \text{ (Kane).}$$

Combinations. *a.* Protochloride of iodine deliquesces in the air and is very soluble in water. (Gay-Lussac.) A solution of the protochloride is obtained when a small quantity of chlorine is passed through water in which an excess of finely divided iodine is diffused. The concentrated solution is dark brownish red; a dilute solution, dark reddish yellow; the former resembles the dry protochloride in its odour and in the other effects which it produces on the body. When exposed to a very low temperature, it deposits a large quantity of a reddish yellow substance which again dissolves on the application of heat. (Kane.)

b. Dissolves in alcohol, forming a yellow solution.

c. Ether separates protochloride of iodine from an aqueous solution, and deposits it unchanged on evaporation. (Dumas.)

b. Terchloride of Iodine.

Formation.—1. By treating iodine with excess of chlorine gas.—2. Finely divided iodine introduced into dry hydrochloric acid gas, forms liquid chloride of iodine, with evolution of heat and ebullition: on cooling, the chloride of iodine crystallizes in long needles. (Serullas.) The reaction is doubtless attended with disengagement of chlorine:

$$IO^5 + 5HCl = ICl^3 + 5HO + 2Cl.$$

A mixture of strong hydrochloric acid and crystallized iodic acid, evolves chlorine and yields terchloride of iodine. (Soubeiran.) When dilute hydrochloric acid is mixed with iodic acid, it instantly turns yellow, and on the addition of oil of vitriol deposits terchloride of iodine. (Serullas.) Chlorine gas is likewise disengaged. (Soubeiran.)

Preparation. Dry chlorine gas is passed over dry iodine for six hours, and in large excess, the mass being gently heated and frequently stirred. (Soubeiran.) Serullas recommends that the mass obtained be treated with a very small quantity of an aqueous solution of terchloride of iodine, to remove any protochloride of iodine which may be present; though he himself adds that the residue, after this treatment, may contain a large quantity of iodic acid.

Properties. Orange-yellow. Crystallizes on cooling after fusion in long needles. (Serullas.) Acts on other substances in the same manner as the protochloride. (Kane.) Decolorizes solution of indigo. (Gay-Lussac.) Does not turn starch blue, except on the addition of an aqueous solution of protochloride of tin.

	Calculation.		Kane.
I	126·0	54·26	54·34
3Cl	106·2	45·74	45·66
ICl^3	232·2	100·00	100·00

	Vol.
Vapour of Iodine	1
Chlorine gas	3

Decompositions.—1. Terchloride of iodine melts at a temperature between 20° and 25°, evolving chlorine gas, which it again absorbs on cooling. (Serullas.)—2. In contact with a very small quantity of water, it is resolved into an insoluble yellowish portion [probably a mixture of terchloride of iodine and iodic acid], and a solution of protochloride and terchloride of iodine [and hydrochloric acid?]. (Serullas.) One portion of the terchloride probably dissolves undecomposed; the rest is resolved into hydrochloric acid, iodic acid, and protochloride of iodine:

$$2ICl^3 + 5HO = 5HCl + IO^5 + ICl.$$

On treating anhydrous terchloride of iodine with an aqueous solution of terchloride of iodine, a small quantity of iodic acid separates, the quantity of which is greatly increased by the addition of alcohol; the same occurs when terchloride of iodine is moistened with water and then treated with absolute alcohol or ether. (*p.* 225.) (Serullas.)

Terchloride of iodine is less readily dissolved by water than the protochloride; the saturated solution may be regarded either as aqueous terchloride of iodine—which is the more probable supposition—or as a mixture of hydrochloric acid and iodic acid containing free iodine; or as a mixture of hydrochloric acid and an acid of iodine which contains 3 atoms of oxygen.

$$5ICl^3 + 15HO = 15HCl + 3IO^5 + 2I;$$
$$\text{or}: ICl^3 + 3HO = 3HCl + IO^3.$$

A similar solution is obtained on passing chlorine gas to saturation, through 1 part of iodine diffused in 4 parts of water, the mixture being kept cool, and the excess of chlorine afterwards removed by a current of atmospheric air. The solution, when saturated with chlorine as completely as possible, has a bright yellow colour, and contains rather more than 3 atoms of chlorine, to 1 atom of iodine, because the water gives rise to the formation of a small quantity of hydrochloric acid and iodic acid. (Soubeiran.) Solution of terchloride of iodine may also be prepared by precipitating an aqueous solution of the protochloride with corrosive sublimate, and distilling the liquid after decanting it from the precipitated iodide of mercury.

When an aqueous solution of terchloride of iodine is gradually mixed with oil of vitriol, and the vessel kept cool, the terchloride separates in the form of a white curdy mass, which afterwards assumes an orange-yellow colour; on heating the mixture, it dissolves, but separates again as the liquid cools; on distilling the mixture, the terchloride passes over. (Serullas.) Ether does not separate terchloride of iodine from an aqueous solution (Dumas); but if protochloride of iodine is also present, the ether takes up terchloride of iodine in company with it, provided the solution is not too dilute. (Serullas.) An aqueous solution of terchloride of iodine neutralized with a fixed alkali, yields metallic chloride, alkaline iodate, and a precipitate of iodine, which redissolves in an excess of alkali in the form of iodide and iodate. (Liebig.)

$$5ICl^3 + 18KO = 15KCl + 3(KO, IO^5) + 2I.$$

On mixing the aqueous solution with an aqueous solution of normal iodate of potash, and then adding alcohol, biniodate of potash is precipitated. (Serullas.) An aqueous solution of terchloride of iodide agitated with a small quantity of oxide of silver, yields chloride of silver and iodic acid; when a larger quantity of oxide of silver is used, the chloride of silver is mixed with iodate of silver. (Serullas.) Iodide of silver is probably formed at the same time,

$$3ICl^3 + 10AgO = 9AgCl + AgI + 2IO^5.$$

Silver leaf is converted by aqueous terchloride of iodine into chloride and iodide of silver. (Serullas.) When aqueous terchloride of iodine is mixed with a small quantity of a solution of protochloride of tin, a precipitate of iodine is obtained, which dissolves on adding a larger quantity of chloride of tin, without separation of needles of protiodide of tin. (Kane.)

Terchloride of iodine unites with metallic chlorides. (Filhol.)

Dry iodine cannot be made to combine with 5 atoms of chlorine (Liebig); iodine diffused in 4 parts of water does not absorb much more than 3 atoms of chlorine, and the yellow solution obtained yields a precipitate of iodine when saturated with alkalis. (Soubeiran.) The same results are obtained when the quantity of water is 8 or 10 times as great as that of the iodine. If, however, the iodine be diffused through a still larger quantity of water, 20 parts for instance (Soubeiran), the iodine combines with 5 atoms of chlorine; the solution in this case is colourless, or merely coloured yellow from excess of chlorine which may be removed by a current of air; it exhibits all the properties of a solution of hydrochloric acid and iodic acid. (Liebig, Soubeiran, L. Thompson.)

$$I + 5Cl + 5HO = IO^5 + 5HCl.$$

A solution of the same kind is obtained on mixing dilute hydrochloric and

iodic acid. It is very acid, smells slightly of chlorine, and slowly decolorizes solution of indigo. (Gay-Lussac.) When it is distilled, hydrochloric acid passes over first; but as the liquid becomes more concentrated, it is again converted [with disengagement of chlorine ?] into a yellow solution of terchloride of iodine [and iodic acid ?]. (L. Thompson.) Oil of vitriol precipitates terchloride of iodine from it (Serullas) and liberates chlorine. (Soubeiran.)

B. *Sulphate of Iodide of Sulphur* ?—1. Formed by distilling iodine with sulphite of lead. The dark red distillate contains excess of iodine.—2. By dissolving iodine in anhydrous wood spirit, saturating the solution with sulphurous acid gas, and distilling off the wood spirit. Very acid and highly corrosive liquid. (Playfair, *Berzel. Jahresber.* 20, 65.)

Chlorine and Bromine.

Chloride of Bromine.

Formed when chlorine gas is passed through bromine, and the vapours which escape condensed by a freezing mixture. Reddish-yellow, very mobile and volatile liquid; emits dark yellow fumes, having the colour of chloric oxide, and a very powerful odour, and causing a flow of tears. The liquid has a hot, unpleasant taste. Metals burn in the vapour, and are converted into chlorides and bromides. (Balard.)

Hydrate of Chloride of Bromine.—1. Chlorine gas is passed through bromine covered with water, whereby the bromine is first dissolved and the liquid afterwards converted into a crystalline mass.—2. A mixture of chloride of bromine and water is cooled to a temperature below 0°.—3. Vapour of chloride of bromine is passed through a moistened glass tube at a temperature between 0° and + 3°.—Light yellow coloured needles or scales, having the same odour and taste as chloride of bromine. The compound melts above 70° (158° F.), forming a pale yellow liquid. It is rapidly decomposed by ammonia into nitrogen gas, chloride of nitrogen, and hydrobromate of ammonia. (Löwig.)

Aqueous solution of Chloride of Bromine.—1. The yellowish solution has the odour and the bleaching properties of anhydrous chloride of bromine, and is resolved by fixed alkalis into metallic chloride and alkaline bromate. (Balard.) At a temperature below 20°, it freezes to a homogeneous mass; when exposed to the sun's rays, it is resolved into aqueous hydrochloric and bromic acids. (Löwig.)

Hydrochlorate of Bromine.—Strong hydrochloric acid dissolves a large quantity of bromine, and forms a solution having the colour, smell, and taste of hydrobromous acid, and like that acid, dissolving gold. (Löwig.)

Bromine yields with *Chloride of sulphur* a beautiful red coloured liquid, which does not conduct electricity unless a small quantity of ether is added to it. (Solly.)

Other Compounds of Chlorine.

A. With Nitrogen.

B. With the metals chlorine forms the *Metallic Chlorides* (*hypothetically anhydrous Muriates*), *Chlorures metalliques* (*Muriates secs.*) *Formation and Preparation*:—1. By contact of a metal with dry chlorine gas. The union of many metals with chlorine is attended with development of light and heat. The following metals burn in chlorine gas at ordinary temperatures. Potassium, in mass; arsenic, antimony, or bismuth, in a state of powder; tin, in the form of tin-foil, after some time; Dutch metal in leaf; copper or nickel, when reduced from the oxide by hydrogen gas to the state of finely divided metallic powders. The following burn when heated: sodium, tungsten, manganese, zinc, tellurium, iron, cobalt, German silver, and mercury (the latter when heated to the boiling point). Lead, silver, gold, and platinum unite indeed with chlorine, but the combination is not, at any temperature, attended with evolution of light and heat. Böttger (*Pogg.* 43, 660) passes chlorine gas through a chloride of calcium tube, to the bottom of a pint or half-pint bottle, till the whole of the atmospheric air is expelled, and then introduces the metal in the form of a wire or bar, a quarter of line in thickness, and wrapt up in Dutch foil, so that the latter, when it takes fire in the gas, may also set fire to the other metals. Treated in this manner, a rod of antimony or bismuth (obtained by running the fused metal into a glass tube) becomes red-hot, runs down in drops, and burns with a brilliant white light and emission of sparks. A well hardened watch-spring wound in a spiral form, burns with incandescence, and produces a dense brownish red cloud: a finer spring emits a more brilliant light and a shower of sparks. Very fine copper wire becomes red-hot, but burns without emission of sparks. Brass wire burns completely, with the most abundant emission of sparks. German silver wire becomes white hot, and throws off melted drops which burst with a splendid light. Wires of zinc, cadmium, lead, fusible metal, nickel, silver, gold, platinum, or palladium, cannot be inflamed in this manner. (Böttger.) A feebly ignited copper wire burns completely in chlorine gas, yielding dichloride of copper in fused drops. (Wöhler, *Berzel. Jahresber.* 19, 215.) —2. Chlorine gas decomposes a great many metallic oxides, sometimes even at ordinary temperatures (*e. g.* oxide of silver) sometimes with the aid of heat (as the fixed alkalis), the products being metallic chloride and oxygen gas. In these cases, one volume of oxygen is usually set free for every two volumes of chlorine absorbed. The above decomposition takes place when the affinity of the chlorine for the metal + that of the oxygen for heat is greater than the affinity of the oxygen for the metal + that of heat for chlorine. (*Sch.* 8.)—3. Many metals, either at ordinary temperatures, or at a red heat, or when aided by the passage of electric sparks, convert hydrochloric acid gas into metallic chloride and a half-volume of hydrogen gas (*p.* 321).—4. Most metallic oxides by contact with hydrochloric acid, yield metallic chlorides and water (*p.* 321).—5. Many metallic oxides, when mixed with charcoal and heated to redness in a tube, are resolved, by a current of chlorine, into metallic chlorides and carbonic oxide or carbonic acid. (Gay-Lussac & Thénard, *Recherches*, 2, 143; Oerstedt, *Pogg.* 5, 132.) This method is especially adapted to the preparation of the compounds of chlorine with the earth-metals. To obtain metallic chlorides in large quantity by this process, Quesneville (*J. Pharm.* 15, 328; also *Schw.* 56, 373) ignites the mixture

of metallic oxide and charcoal in a tubulated earthen retort instead of a porcelain tube, and passes the chlorine into the mixture through a tube which fits into the tubulure of the retort. When the chloride is liquid, he receives it in a Woulfe's bottle connected with the neck of the retort by means of a bent tube-funnel; and when it is solid, in a glass globe which runs out at the bottom into an elongated point, and has an opening above and two openings at the sides; through one of the side openings the neck of the retort enters; the opposite opening serves for the passage of an iron wire to clear out the neck of the retort when stopped up with the metallic chloride.—6. Metallic chlorides are formed in the various decompositions of hypochlorites, chlorites, chlorates, and perchlorates.—7. One metallic chloride may be converted into another by the action of single or double affinity. Chloride of mercury yields with antimony: chloride of antimony and metallic mercury; and with sulphide of antimony: chloride of antimony and sulphide of mercury. (*Sch.* 45.)

Some metallic chlorides are liquid at ordinary temperatures; and these are very volatile: *Metallic oils* (the chlorides of tin, arsenic, antimony); some are solid, though at the same time very fusible, and generally volatile at a red heat; the softer of these are called *Metallic butters* (the chlorides of antimony, bismuth, zinc) the more solid, *Horn-metals* (*e.g.* horn-silver, horn-lead.) Those metallic chlorides which are not decomposed by heat, are, almost without exception, more volatile than the metals from which they are formed.

A few metallic chlorides, when ignited out of contact of air, are resolved into metal and chlorine gas (the chlorides of gold and platinum). Some give up only a portion of their chlorine (protochloride of copper). Others again are not decomposed by simple ignition; but when ignited in the air, are resolved into metallic oxides and chlorine gas (such is the case with the chlorides of manganese and iron; the chlorides of barium, strontium, and calcium are also to a very small extent converted into oxides by this treatment.) Most chlorides remain undecomposed in either case. Metallic chlorides which are not decomposed by heat alone, likewise resist the action of charcoal at a white heat, because carbon does not form any inorganic compound with chlorine. (Inasmuch, however, as the charcoal usually contains a small quantity of hydrogen, a small portion of the chloride may be converted, at the beginning of the action, into metal and hydrochloric acid.) But as soon as the ignited mixture is brought in contact with aqueous vapour, the oxygen of which has considerable affinity for the charcoal, and the hydrogen for the chlorine, decomposition takes place, —*viz.*, with the chlorides of silver and mercury—into carbonic acid or carbonic oxide, hydrochloric acid, and metal. (Gay-Lussac & Thénard.) (*Sch.* 78);

$$AgCl + HO + C = Ag + HCl + CO.$$

The contrary results obtained by Lampadius, which do not accord with any theory (*Gilb.* 73, 143), may be attributed to the porosity of the earthen retorts which he used, and indeed are altogether refuted by Döbereiner's experiments. (*Gilb.* 73, 227.) No metallic chloride is decomposed by heating with sulphur; phosphorus, on the contrary, separates the chlorine from several of these compounds. (H. Rose, *Pogg.* 27, 116.)

Those metallic chlorides which are not decomposed by heat alone, *e. g.* the chlorides of the alkali-metals, silver and mercury, likewise resist decomposition when heated to whiteness (in the absence of moisture) with vitrefied boracic acid, vitrefied phosphoric acid containing lime, or with silica, glucina, or alumina—substances which, though they have more or

less affinity for metallic oxides, have no affinity for the metals themselves, or for chlorine. As soon, however, as aqueous vapour comes in contact with the ignited mixture, its oxygen combines with the metal, forming a metallic oxide, which is taken up by the above mentioned acids or earths, and the hydrogen of the water escapes in union with the chlorine, as hydrochloric acid gas. (Gay-Lussac & Thénard, Davy.) (*Sch.* 58.)

$$NaCl + HO + nSiO^2 = NaO, nSiO^2 + HCl.$$

But when the vapour of anhydrous sulphuric acid—which retains its oxygen less forcibly than boracic or phosphoric acid—is passed over ignited common salt, sulphate of soda is formed, and a mixture of equal volumes of chlorine and sulphurous acid gas is evolved. (*Sch.* 74.)

$$NaCl + 2SO^3 = NaO, SO^3 + SO^2 + Cl.$$

The very light yellow-coloured gaseous mixture which escapes, is absorbed by water in the form of hydrochloric and sulphuric acids, one atom of chlorine taking one atom of hydrogen from the water, and the atom of oxygen thus set free being taken up by the sulphurous acid. Hence Sertürner concluded that hydrochloric acid exists already formed in the gaseous mixture. (*Vid.* Sertürner, *Gilb.* 72, 109; 73, 213;—Döbereiner, *Gilb.* 72, 331;—C. G. Gmelin. *Schw.* 37, 442;—L. Gmelin, *Gilb.* 73, 109.) Nitric acid likewise disengages chlorine from many metallic chlorides, inasmuch as it oxidizes the metals, and then combines with the metallic oxide formed.

Hydrated boracic, phosphoric, sulphuric and arsenic acid, decompose most metallic chlorides, sometimes at ordinary temperatures, sometimes with the aid of heat, the products being hydrochloric acid and a compound of the metallic oxide with the oxygen acid. The compounds of the light metals,—manganese, zinc, tin, iron, and cobalt—with chlorine, are decomposed by oil of vitriol, even at ordinary temperatures; those of antimony, bismuth, and copper, only with the aid of heat. (A. Vogel.) Protochloride of mercury is not decomposed at any temperature. Metallic chlorides when mixed with peroxide of manganese or peroxide of lead, and heated with oil of vitriol, evolve chlorine gas; and when mixed with chromate of potash and distilled with oil of vitriol, they yield a dark bluish red distillate of chromate of terchloride of chromium. A bead of microcosmic salt nearly saturated with oxide of copper, imparts a blue colour to the blow-pipe flame on the addition of a metallic chloride. (Berzelius.)

Hydrated Metallic Chlorides or *Hydrochlorates* (*Chlorwasserstoffsäure Salze, Muriates, Chlorhydrates*).

All metallic chlorides are soluble in water, excepting chloride of silver, dichloride of copper, dichloride of mercury, protochloride of gold, and protochloride of platinum. These solutions may be regarded either as aqueous metallic chlorides or as aqueous hydrochlorates of metallic oxides. The same solutions are obtained by treating metallic oxides with aqueous hydrochloric acid, and, in many cases, by treating a metal with aqueous hydrochloric acid, hydrogen gas being evolved.

$$Zn + HCl = ZnCl + H$$
$$\text{or: } Zn + HO + HCl = ZnO, HCl + H.$$

Further, by treating many metals with a mixture of aqueous hydrochloric and nitric acids.

$$3Cu + 3HCl + NO^5 = 3CuCl + 3HO + NO^2;$$
$$\text{or: } 3Cu + 3HCl + NO^5 = 3(CuO, HCl) + NO^2.$$

These solutions when cooled and evaporated, deposit either anhydrous metallic chlorides (as in the case of chloride of sodium) or hydrated crystals, which may be regarded as hydrated metallic chlorides or as salts of hydrochloric acid: they generally also contain an additional quantity of water. Thus, chloride of barium crystallizes from an aqueous solution in the form of $BaCl+2HO=BaO, HCl+HO$; chloride of calcium crystallizes with six atoms of water, ($CaCl+6HO=CaO, HCl+5HO$.) These hydrated crystals, when strongly heated, either give off water and are converted into metallic chlorides, or they evolve hydrochloric acid and leave metallic oxides: such is the case with a solution of magnesia or alumina in hydrochloric acid.—(On the question, whether the metallic chlorides are converted into hydrochlorates or not, in contact with water, *vid.* pp. 10—13.) H. Rose (*Pogg.* 55, 533,) is of opinion that the mode of action varies with the nature of the chloride. According to Rose, a metallic chloride dissolves without alteration, when the metal which it contains is capable of forming a salifiable base with oxygen (the alkali-metals, mercury, &c.); on the contrary, it dissolves in the form of hydrochlorate of the oxide, when the latter has a more acid character (silicium, titanium, tin, arsenic, antimony and bismuth). The solution of the former class of metallic chlorides is generally attended with production of cold, that of the latter, always with evolution of heat; and by this character the two classes of metallic chlorides may be distinguished from each other, a few cases only excepted. Against this, the advocates of the theory of hydrogen salts of metallic oxides may allege:—1. That the metallic chlorides of the former class are precisely those which, *à priori*, may be expected to be most easily decomposed by water, inasmuch as that class includes the very metals whose affinity for oxygen, [but at the same time, also, for chlorine] is the greatest: moreover, the predisposing affinity of the salifiable oxide for hydrochloric acid, and *vice versâ*, may be expected to facilitate the formation of these compounds.—2. That when the affinity of chlorine for the metal + that of hydrogen for oxygen is nearly equal to the affinity of the metal for oxygen + that of chlorine for hydrogen + that of the metallic oxide for hydrochloric acid, decomposition takes place attended with slight evolution of heat; but the rise of temperature thus produced is more than counterbalanced by the heat which is rendered latent in the passage of the solid substance to the liquid state (as with common salt). On the other hand, the more the latter sum of affinities exceeds the former —the more, that is to say, the affinity of a metal for oxygen exceeds its affinity for chlorine—the greater will be the rise of temperature produced by its solution. Rose enumerates chloride of calcium among the metallic chlorides which are not decomposed by solution, notwithstanding that it evolves great heat by contact with water; and explains this anomaly by supposing that the first atoms of water combine more intimately with the salt, in the form of water of crystallization. But if this explanation is to be admitted as satisfactory, and especially if it is to extend to those cases in which, by the use of a larger quantity of water, the mixture is retained in the liquid state and prevented from crystallizing, the application of change of temperature to determine whether a metallic chloride is or is not decomposed by solution in water—even supposing the theory to be well founded—will be reduced within very narrow limits.

Aqueous solutions of metallic chlorides precipitate chloride of lead from lead-salts moderately concentrated, dichloride of mercury from mercurous salts, and chloride of silver from silver salts, even when largely diluted: the precipitates are white. Chloride of silver and dichlo-

ride of mercury, when precipitated from solutions somewhat concentrated, assume a curdy form; when the liquid is much diluted, they produce a milky opalescence. Chloride of silver acquires a violet tint when exposed to light; it is insoluble in dilute nitric acid, but ammonia, even when dilute, dissolves it readily (thereby distinguished from iodide or bromide of silver). If common salt be dissolved in such quantities of water, that one part of chlorine shall be contained in the following quantities of liquid, the different solutions exhibit the annexed reactions with nitrate of mercurous oxide and nitrate of silver: 50,000 parts of water: with mercury, pulverulent precipitate; with silver, slight milky turbidity; 100,000 parts of water: mercury, slight precipitate; silver, slight turbidity;—200,000 parts of water: mercury, turbidity after a few minutes; silver, immediate slight cloud;—400,000 parts of water: mercury, very slight turbidity after some minutes; silver, very slight turbidity;—800,000 parts of water: mercury, opalescence after some time; silver, very faint opalescence;—1,600,000 parts of water: mercury, scarcely preceptible opalescence after some time; silver, scarcely perceptible opalescence. With solution of sal-ammoniac, the silver solution behaves in a similar manner, and gives a barely perceptible cloud, even with 3,200,000 parts of water; with mercury, however, the reaction ceases with 400,000 parts of water to one part of chlorine. (Lassaigne, *J. Chim. med.* 8, 518.) A mixture of a metallic chloride with sulphate of copper dissolved in water, gradually blackens a polished plate of silver.

Some metallic chlorides (*e. g.* the chlorides of ammonium, potassium, and sodium) combine with terchloride of iodine. (For the preparation of these compounds, see more especially the chapter on *Potassium.*) They may be regarded as chlorine salts, in which the terchloride of iodine plays the part of an acid, *e. g.* KCl, ICl^3.

Some metallic chlorides combine with hydrochloric acid. Thus, the dichloride of copper, which is insoluble in water, dissolves in strong hydrochloric acid; and corrosive sublimate is much more soluble in hydrochloric acid than in water. These compounds may be considered either as chlorine-salts, in which the hydrochloric acid is the acid and the metallic chloride the base; or, according to the other theory (since water is present), as acid hydrochlorates of metallic oxides.

Some metallic chlorides are capable of uniting with the oxides of the same metals: *Oxychlorides, Oxychlorures, e. g.* $CrCl^3, 2CrO^3$,—$3PbO, PbCl$, and $5SbO^3, SbCl^3$. (or as more recently determined by Malaguti and Johnston, $9SbO^3, 2SbCl^3$.) When water is added to these compounds, hydrated oxychlorides—or, according to the other view—basic hydrochlorates of the oxides, are produced. Thus, atacamite is:

$$3CuO, CuCl + 4HO \text{ or } 4CuO, HCl + 3HO.$$

Many metallic chlorides combine with each other: *Metallic Chlorine salts.*—For instance, the chlorides of mercury, platinum, and gold, and other electro-negative chlorides, combine with the chlorine compounds of the alkali-metals and other positive metals. In these compounds, Bonsdorff regards the chloride of mercury, &c., as the acid, and the chloride of potassium, &c., as the base. According to the same authority, the aqueous solutions of the chlorides of calcium, magnesium, manganese and zinc, turn logwood blue and are therefore of a basic nature; the chlorides of barium and strontium give the same reaction in a slight degree; chloride of potassium and chloride of sodium, not at all. (Bonsdorff.) Compare the contrary observations of H. Rose (*Pogg* 55, 552).

Many metallic chlorides are capable of uniting with ammonia in definite proportions.

Many again are soluble in alcohol, ether, volatile oils, &c. and a few are capable of entering into organic compounds.

Antichloristic Theory.

Lavoisier's discovery, that most acids contain oxygen, led to the supposition, that the acids which, up to that time, had not been decomposed —muriatic acid, for example—derived their acid properties from the presence of the same element. Muriatic acid was therefore regarded as a compound of oxygen with the unknown radical, *Muriatum*, or *Murium*; and chlorine, or oxygenised muriatic acid, was supposed to contain the same radical united with a larger quantity of oxygen. This so-called muriatum, however, could not be isolated. Moreover, it was found that the dryest muriatic acid gas, when brought in contact with red-hot metals, evolves a large quantity of hydrogen; and that 1 volume of dry chlorine gas with 1 volume of dry hydrogen forms two volumes of perfectly dry muriatic acid gas. From these two facts it was concluded that 1 volume of chlorine (or oxymuriatic acid) gas contains a half volume of oxygen, which, in the formation of muriatic acid gas, combines with 1 volume of hydrogen; and that muriatic acid gas is an intimate compound, in equal numbers of atoms, of water and a not yet isolated *anhydrous muriatic acid*, which may be called *hypothetically anhydrous muriatic acid*, to distinguish it from ordinary dry or anhydrous muriatic acid gas. Berzelius formerly arranged the various degrees of oxidation in the series as follows:

1 At. Murium = 11·4, takes up of Oxygen: At.	And forms therewith:	*Antichloristic Names.*	*Chloristic Names.*
2 = 16	27·4	Hyp. Anhyd. Muriatic acid	
3 = 24	35·4	Oxymuriatic acid	Chlorine.
4 = 32	43·4	Euchlorine	Chlorous oxide.
6 = 48	59·4	?	Chloric oxide.
8 = 64	75·4	Hyperoxymuriatic acid	Chloric acid.
10 = 80	91·4	?	Perchloric acid.

Muriatic acid gas is a compound of 1 At. hypothetically anhydrous muriatic acid = 27·4, with 1 At. water = 9, making together 36·4 (MuO^2 + HO). Charcoal cannot decompose the water contained in muriatic acid gas, not even at a white heat, because the great affinity of hyp. anhydrous muriatic acid for the water protects it from decomposition. Neither can charcoal withdraw from oxymuriatic acid (MuO^3) its third atom of oxygen; because the oxygen has a stronger affinity for hyp. anhydrous muriatic acid than for carbon. Phosgene gas is a compound of hyp. anhydrous muriatic acid with carbonic acid (MuO, CO^2); in this case, carbonic oxide is able to abstract the third atom of oxygen from oxymuriatic acid, and form carbonic acid, because the affinity of hyp. anhydrous muriatic acid for carbonic acid is likewise very great. Our terchloride of phosphorus is hypothetically dry muriate of phosphorous acid ($PO^3, 3MuO^2$); pentachloride of phosphorus is hyp. anhydrous muriate of phosphoric acid ($PO^5, 5MuO^2$). The phosphorus burns in the third atom of oxygen of the oxymuriatic acid gas, forming phosphorous or phosphoric acid, which then enters into intimate combination with the separated anhydrous muriatic acid. Similarly, the two chlorides of

sulphur may be regarded as compounds of hyp. anhydrous muriatic acid with hyposulphurous acid and another lower oxide of sulphur, not yet isolated, containing 2 At. S and 1 At. O. In the same manner, also, the oxychloride of bisulphide of carbon is to be regarded as a compound of 2 At. hyp. anhydrous muriatic acid with 1 At. carbonic acid and 1 At. sulphurous acid (CO^2, SO^2, MuO^2). Water decomposes these compounds by converting the hyp. anhydrous muriatic acid into muriatic acid gas, which has no longer any affinity for the substance previously combined with the hypothetically anhydrous muriatic acid. Chloride of nitrogen, which will be described in the next chapter, is, according to this theory, a compound of hyp. anhydrous muriatic acid with nitrous acid ($NO^3, 3MuO^2$). Metallic chlorides are hyp. anhydrous muriates of metallic oxides; for the metal, when immersed in oxymuriatic gas, burns in its third atom of oxygen and is converted into an oxide, which then combines with the remaining hyp. anhydrous muriatic acid and forms a hyp. anhydrous muriate of that oxide. The same compounds are formed when various metallic oxides are brought in contact with oxymuriatic acid gas, the third atom of oxygen then escaping in the form of gas and the remaining hyp. anhydrous muriatic acid combining with the oxide. A hyp. anhydrous metallic muriate may also be formed, with evolution of hydrogen, by contact of a metal with muriatic acid gas, the oxidation being in this case produced by the water contained in the muriatic acid gas. Lastly, when muriatic acid gas is brought in contact with oxide of lead, the water contained in the gas is set at liberty, and the hyp. anhydrous muriatic acid combines with the oxide of lead: the water is an educt, according to the antichloristic theory; whereas according to the chloristic theory it is a product. No other acid has so great an affinity for metallic oxides as muriatic acid; and therefore its salts resist the decomposing action of all other acids (of boracic acid, at a red heat, for example); but if water is present, decomposition takes place; because hyp. anhydrous muriatic acid has likewise a great affinity for that substance, so that the affinity of the foreign acid for the metallic oxide, together with the affinity of the hyp. anhydrous muriatic acid for the water, overcomes the affinity of the hyp. anhydrous muriatic acid for the metallic oxide. Common salt is decomposed by sulphuric acid, because the affinity of the hyp. anhydrous muriatic acid for the oxygen of a portion of the sulphuric acid, together with the affinity of the soda for the remaining portion of that acid, is greater than the affinity of the hyp. anhydrous muriatic acid for the soda, together with that of the sulphurous acid for the third atom of oxygen. Charcoal does not decompose the hypothetically anhydrous muriates, because the greater affinity of hyp. anhydrous muriatic acid for the metallic oxide—oxide of silver, for example—protects the oxide from the decomposing action of the charcoal; but if vapour of water is also present, so that the hyp. anhydrous muriatic acid can combine with it and form muriatic acid gas, the charcoal is then able to deprive the metallic oxide of its oxygen and form carbonic acid.

The formation of a muriate and hyperoxymuriate (chlorate) of an alkali, when oxymuriatic acid comes in contact with the aqueous solution of an alkali, is effected by 5 atoms of oxymuriatic acid giving up their third atom of oxygen to a sixth atom of oxymuriatic acid, which is thereby converted into hyperoxymuriatic acid.

This system is more uniform than the modern *Chloristic Theory*, inasmuch as it supposes that all acid and basic substances contain oxygen—

which however is not the case with the hydrosulphuric, hydrotelluric, hydrocyanic, and other undoubted hydrogen-acids. Moreover, the theory assumes the existence of two substances which are purely hypothetical and cannot be obtained in the separate state, viz., *murium* and *hypothetically anhydrous muriatic acid.* Both theories, however, admit of being consecutively carried out; and, however opposed they may be to each other, neither of them is contradicted by a single direct experiment. But the chloristic theory is by far the simpler of the two, and more supported by analogy than the antichloristic. (For the arguments formerly adduced by Berzelius in favour of the antichloristic theory, *vid. Gilb.* 50, 356; also *Schw.* 14, 66.)

Berzelius applied the same views to iodine as to chlorine, regarding iodine as a compound of an acid-radical with 3 atoms of oxygen. He assumed 102 as the atomic weight of the iodine-radical; and supposed that this radical, in combination with 2 atoms of oxygen = 16, formed *hypothetically anhydrous hydriodic acid,* which, by taking up an atom of water = 9, is converted into hydriodic acid gas; 102 iodine-radical combines with 3·8 = 24 oxygen to form iodine, and with 8·8 = 64 oxygen to form iodic acid. Iodide of phosphorus and iodide of sulphur would, according to the same theory, be regarded as compounds of hypothetically anhydrous hydriodic acid with certain oxides of phosphorus and sulphur; and the metallic iodides, as compounds of hypothetically anhydrous hydriodic acid with metallic oxides.

Chapter XI.

FLUORINE.

Scheele, *Opusc.* 2, 1 and 242; *Crell. Chem. J.* 2, 192, and *Crell. Ann.* 1786, 1, 3.
Wiegler, *Crell. N. Entdeck.* 1, 3.
Bucholz, *Crell. N. Entdeck.* 3, 50.
Gay-Lussac & Thénard, *Recherches,* 2, 1; also *Ann. Chim.* 69, 204; also *N. Gehl,* 8, 485; also *Gilb.* 32, 1.
Sir H. Davy, *Phil. Trans.* 1809; also *Schw.* 2, 57; also *Gilb.* 35, 452,—*Phil. Trans.* 1813, 263; also *Ann. Chim.* 88, 271.
J. Davy, *Phil. Trans.* 1812, 352; also *Ann. Chim.* 86, 178.
Berzelius, *Pogg.* 1, 1 and 169; 2, 111; 4, 1 and 117.
Otto Unverdorben, *N. Tr.* 9, 1, 22.

History. The process of etching on glass with fluor-spar was known to Schwankhard, of Nuremberg, as early as 1670. Marggraf, in 1764, observed that a glass retort in which he had heated fluorspar with sulphuric acid was corroded, and a white sublimate formed. Scheele, in 1771, first discovered that fluor-spar is a compound of lime with a peculiar acid; he likewise prepared that acid from it, both in the state of aqueous solution, by using a tin retort to distil it, and likewise in the form of gaseous fluoride of silicium; but Priestley was the first who collected that gas over mercury. Gay-Lussac & Thénard, in 1808, first prepared anhydrous hydrofluoric acid and discovered fluoboric gas.

John Davy, in 1812, investigated various relations of fluoride of boron and fluoride of silicium. Up to that time, hydrofluoric acid had been regarded as a compound of oxygen with an unknown combustible base. *Fluorium*, which Gay-Lussac & Thénard and Sir Humphry Davy in vain endeavoured to separate from fluosilicic acid gas by means of potassium. Ampère, in 1810, first applied the chloristic theory to the relations of hydrofluoric acid, considering that acid as a compound of hydrogen with an unknown substance, *fluorine*, and fluor-spar as a fluoride of calcium. This theory was supported by Sir Humphry Davy by a variety of experiments, and adopted by him and by many other chemists. Finally, in 1824, the chemical history of the fluorine compounds was greatly extended by the comprehensive researches of Berzelius.

Sources. Not abundant: found chiefly in fluor-spar; also in fluoride of cerium, basic hydrofluate of cerium, topaz, cryolite, warwickite, and yttrocerite; and in small quantities in fluor-apatite, wagnerite, amblygonite, wavellite, leucophane, lepidolite, many kinds of mica and apophyllite, in carpholite, chondrodite, hornblende, and pyrochlor. According to Breithaupt and Harkort (*Pogg.* 9, 179), it likewise occurs in felspar and the allied minerals. Moreover, in bones, teeth, and human urine. The late remarkable assertion of Rees (*Phil. Mag. J.* 15, 459,) that human bones, the enamel of the teeth, and ivory, do not contain fluorine has been refuted by Erdman. (*J. pr. Chem.* 19, 446.)

Of fluorine in the separate state we know but little; its property of corroding vessels of almost every description renders its separation a matter of great difficulty. The following are the attempts which have hitherto been made to effect the preparation of pure fluorine.

The fluorides of potassium, sodium, mercury, and silver, may be decomposed by chlorine; but if the decomposition is performed in glass vessels, the fluorine, as it is separated, acts upon the silica contained in the glass, so that fluoride of silicium is formed and oxygen set free. If platinum vessels are employed, the metal becomes covered with a red-brown powder (fluoride of platinum?); if the platinum vessel is coated internally with fused chloride of potassium, the decomposition of the fluoride is attended with the production of a gas which attacks glass, and has a peculiar odour, more disagreeable than that of chlorine. (H. Davy.)

Aimé (*Ann. Chim. Phys.* 55, 443; also *Pogg.* 32, 576; also *J. pr. Chem.* 2, 469), passed chlorine gas, in the cold, over fluoride of silver contained in glass vessels which were covered with a coating of caoutchouc. Hydrofluoric acid was produced and the caoutchouc carbonized.

Bandrimont (*J. Chim. Med.* 12, 374; also *J. pr. Chem.* 7, 447), passed gaseous fluoride of boron over ignited red lead, and conducted the gaseous fluorine which was evolved into a dry glass vessel. He also heated fluor-spar in a glass vessel with manganese and oil of vitriol; whereupon fluorine gas was evolved mixed with gaseous fluoride of silicium and vapour of hydrofluoric acid. In both cases he obtained a yellowish brown gas, which smelt like chlorine and also like burnt sugar, decolorized solution of indigo, did *not* attack glass, but combined with gold and platinum.

G. J. Knox and Th. Knox (*Phil. Mag. J.* 9, 107; also *J. pr. Chem.* 9, 118), heated fluoride of mercury in a vessel of fluor-spar, till a glass plate laid on the top no longer became covered with drops of water; then passed dry chlorine gas into the vessel through a bent glass tube drawn out to a point at the end; closed the vessel tightly, when full of chlorine, with a plate of fluor-spar; and applied heat to the bottom. Protochloride of mercury sublimed, and the vessel was filled with a yel-

lowish green gas, which did not fume in contact with air, and therefore did not contain hydrofluoric acid, but rapidly corroded a glass plate laid on the top of the vessel. Fluoride of lead was found not to be decomposed by chlorine, even with the aid of heat.

G. J. Knox (*Phil. Mag. J.* 16, 192, *also J. pr. Chem.* 20, 172), filled a vessel of fluor-spar half full of anhydrous hydrofluoric acid, and closed it with a cover of fluor-spar having three holes in it. Through the middle aperture, a platinum wire forming the negative electrode of a sixty-pair battery, was passed into the acid; through one of the lateral apertures, a piece of charcoal, freed from iron and silica by boiling in nitric and in hydrofluoric acid (as otherwise, fluoride of iron and fluoride of silicium would have been formed), was introduced to form the positive electrode. The other lateral aperture served to introduce various substances, for the purpose of observing the effect produced upon them by the fluorine gas which might be evolved. A large quantity of hydrogen gas was evolved on the platinum wire; litmus paper introduced through the side opening was bleached in two hours (hydrofluoric acid does not bleach litmus); gold was attacked and turned brown, after the battery had been acting for fifteen hours. The gas, when passed, as it was evolved, through a tube of transparent fluor-spar, was found to be colourless. Also, when melted fluoride of lead contained in a bent glass tube (*App.* 5), was decomposed by means of a cathode of platinum and an anode of charcoal, a considerable number of gas-bubbles were evolved at the anode; the gas immediately acted on the glass, and consequently did not bleach litmus paper.

¶. Louyet (*Compt. Rend.* 22, 960), decomposed fluoride of silver, in Knox's apparatus, by means of chlorine or iodine, and obtained a gas which was colourless in thin strata; did not bleach vegetable colours; decomposed water rapidly; acted but slowly upon glass, but attacked most metals; gold and platinum, however, were not attacked by it. ¶.

Fluorine must, at all events, be a permanent gas, since it forms gaseous compounds with boron and silicium. (I, 86.)

Atomic weight of fluorine = 19 (H = 1), or 237·50 (O = 1.) Louyet, (*Ann. Chim. Phys.* 25, 291.)

Compounds of Fluorine.

Fluorine and Hydrogen.

Hydrofluoric Acid.

Fluoric acid, Flussspathsäure, Spathsäure, Fluorwasserstoffsäure, Acide fluorique, Acide hydrofluorique, Acide fluorhydrique.

Preparation. One part of pounded fluor-spar, free from silica, is heated in a leaden or platinum retort (the former must not be soldered with tin), with 2 parts of oil of vitriol, a receiver of lead or platinum being adapted without luting to the retort, and surrounded with ice. (Gay-Lussac & Thénard.)

$$CaF + HO,SO^3 = CaO,SO^3 + HF.$$

If the fluor-spar contains silica, fluosilicic acid gas passes over, being evolved in gas-bubbles, even before the mixture is heated; if it contains galena, hydrosulphuric acid and sulphurous acid pass over, and the distillate is clouded with sulphur. (Berzelius.) The product must be preserved in close vessels of gold, platinum, or lead free from tin.

Properties. Transparent and colourless liquid, of specific gravity 1·0609. (H. Davy.) Does not solidify at − 20°. (Gay-Lussac & Thénard.) Refracts light very feebly. (Wollaston.) Boils at comparatively low temperatures—according to Berzelius, not much above 15°.—Has a pungent odour, and acts very injuriously on the respiratory organs; even the vapour produces pains under the nails. Small drops placed upon the skin produce white spots, which rise up into pustules and are attended with violent pain, often exciting vulnerary fever. The application of caustic potash solution, followed by emollient poultices, is useful in these cases; the pustules should also be opened. The acid reddens litmus strongly. (Gay-Lussac & Thénard.)

	Calculation.		Berzelius.
F	18·7	94·92	94·95
H	1	5·08	5·05
HF	19·7	100·0	100·0

(HF = 6·24 + 116·90 = 123·4. Berzelius.)

¶. According to Louyet, the acid obtained by the action of oil of vitriol on fluor-spar is a hydrate; and the true anhydrous acid can only be obtained by distilling this hydrate with anhydrous phosphoric acid. A gaseous product is then obtained which is quite free from water, and does not liquefy at − 12° (+ 10·4° F.) under the ordinary atmospheric pressure. It fumes very strongly in the air, but has scarcely any action upon glass. Louyet is of opinion that it might be collected over mercury in perfectly dry glass vessels. ¶.

Decompositions.—1. In the circuit of the voltaic battery, hydrofluoric acid yields hydrogen gas at the negative pole, while the positive platinum wire becomes corroded with a brown mass (of fluoride of platinum?) *H. Davy.*—2. Potassium, sodium, unignited silicium, tantalum, zinc, iron, and manganese, brought in contact with this acid, produce metallic fluorides and hydrogen gas: in the case of potassium, the action is attended with explosion and vivid combustion. (Gay-Lussac & Thénard; Berzelius.)—3. With lime, the acid forms fluoride of calcium and water, great rise of temperature attending the action. In contact with silica (*e. g.* with glass), it becomes hot, boils up, and is converted into gaseous fluoride of silicium, nothing but a small quantity of aqueous hydrofluosilicic acid remaining. (Gay-Lussac & Thénard.) With most other metallic oxides, also, it forms water and a fluoride of the metal, (or a hydrofluate of the oxide.)—Not decomposed by chlorine, oil of vitriol, or hydrochloric acid.

Combinations. a. Aqueous Hydrofluoric Acid. The affinity between water and hydrofluoric acid is very strong; hence the acid fumes in the air. The act of combination is attended with a development of heat which raises the liquid to the boiling point. With a certain proportion of water, the specific gravity of the liquid acid is as high as 1·250. (H. Davy.) According to Berzelius, the hydrated acid is best prepared by gradually and gently heating a mixture of fluor-spar and oil of vitriol, in a leaden bottle to the mouth of which a bent leaden tube is adapted by means of a stopper also of lead, the joints being made air-tight with oil of vitriol or melted caoutchouc; the other end of the bent tube dips just below the surface of water contained in a leaden bottle or platinum crucible surrounded with ice. The acid obtained by this process may be freed from silica, which is almost always present in fluor-spar,

by dropping into it a solution o fluoride of potassium, as long as a gelatinous precipitate of fluoride of silicium and potassium is produced, (or by adding pounded fluoride of hydrogen and potassium, as long as it dissolves)—then pouring off the clear liquid and distilling in platinum vessels. The acid may be preserved in bottles of gold, platinum, or lead, having a leathern collar soaked in wax laid upon the neck, and then a cap screwed on. A dilute solution, not required to be quite free from silica, may also be kept in glass vessels coated inside with wax.

Transparent, colourless, thin liquid, which fumes in the air when concentrated; when heated, it gives off hydrofluoric acid, and is thereby rendered weaker.

b. With Peroxide of Hydrogen. (II. 78.)

c. With Salifiable Bases, forming salts called *Hydrofluates.* (Vid. *Metallic Fluorides.*)

Fluorine and Boron.

A. Fluoride of Boron. BF^3.

Fluoboric gas, Fluorborongas, flussboraxsaures Gas, Gas fluorborique.

Preparation.—1. One part of vitrefied boracic acid and 2 parts of fluor-spar free from silica are heated to whiteness in a wrought iron gun-barrel placed in an inclined position (Gay-Lussac & Thénard) (*Sch.* 107).

$$3CaF + 7BO^3 = 3(CaO, 2BO^3) + BF^3.$$

—2. One part of vitrefied boracic acid, 2 of fluor-spar, and 12 of oil of vitriol, are gently heated in a glass vessel. (J. Davy). Ferrari (*J. Pharm.* 19, 48) uses 1 part of vitrefied boracic acid, 1 of fluor-spar, and 20 of oil of vitriol. The residue in the second process consists of sulphate instead of borate of lime. According to Berzelius, the gas prepared by method 2, contains a large quantity of fluoride of silicium (proceeding from the silica mixed with the fluor spar, and from the glass vessel), which can only be imperfectly separated by contact with crystallized boracic acid. The gas is collected over mercury.

Properties. Colourless gas. Specific gravity (I. 280). Incombustible, does not support combustion; has a pungent odour like that of fluoride of silicium; very suffocating. Reddens litmus paper strongly. Chars organic substances rapidly. In contact with moist air it forms a very thick, white cloud. When subjected to the action of the carbonic acid bath in vacuo, it condenses to a clear, colourless liquid, which, even at that temperature, is as mobile as warm ether. (Faraday.)

Calculation.

B	10·8	16·14	16·24
3F	56·1	83·86	83·76
BF^3	66·9	100·00	100·00

	Vol.	Sp. gr.		Vol.	Sp. gr.
Vapour of Boron?	1	0·7487	=	½	0·3744
Fluorine gas?	3	3·8892	=	1½	1·9446
Fluoboric gas	2	4·6379	=	1	2·3190

(BF^6 = 136·20 + 6 . 116·90 = 837·60. Berzelius.)

Decompositions.—1. By water into hydrofluoric and boracic acid, 3 At. hydrogen from the water combining with 3 atoms of fluorine, and 3 atoms of oxygen with 1 atom of boron.—2. Potassium heated in fluoboric gas burns (as soon as the black crust which first forms has burst) with a bright, reddish flame; absorbs a quantity of the gas, the volume of which is three times as great as that of the hydrogen which the potassium would liberate from water; and is converted into a brown fusible mass, which appears to be a mixture of boron and fluoride of potassium, and is separated by water—with evolution of a small quantity of hydrogen gas—into fluoride of potassium or hydrofluate of potassa which dissolves, and boron which remains behind. Sodium behaves in the same manner, excepting that the combustion is more vivid and a larger quantity of gas is absorbed. (Gay-Lussac & Thénard.) Red-hot iron has no action on this gas.—3. Burnt lime absorbs fluoboric acid quickly, especially when heated; the resulting mass is fusible, and when treated with oil of vitriol, evolves fluoboric gas. (J. Davy, *N. Ed. Phil. J.* 17, 246.) [In this case, a mixture of fluoride of calcium, and borate of lime is probably formed. $4CaO + BF^3 = 3CaF + CaO, BO^3$.]

Combinations. *a.* With ammonia. *b.* With metallic fluorides, forming compounds called *Metallic Fluoborides.* (Vid. *Metallic Fluorides.*)

B. Hydrofluates of Boracic Acid.

a. Fluoboric Acid. $BO^3, 3HF$.

Formation. By saturating water with fluoboric acid gas. Water, at ordinary temperatures absorbs about 700 measures of fluoboric gas (J. Davy); according to Gay-Lussac & Thénard, about the same volume as of hydrochloric acid gas. The absorption is rapid, and attended with great rise of temperature ($BF^3 + 3HO = BO^3 + 3HF$).

Preparation.—1. The fluoboric gas as it is evolved, is passed through a bent tube dipping under mercury which is covered with a small quantity of water. (Thénard.) If the end of the tube were to dip into the water, the rapid absorption of the gas would cause the liquid to pass back into the generating vessel.—2. Boracic acid is dissolved in aqueous hydrofluoric acid, and the solution concentrated by evaporation till the compound begins to evaporate unchanged. (Berzelius.)

Properties. The solution formed by the absorption of 700 measures of the gas has a specific gravity of 1·770; it is colourless, fuming, and oily, very corrosive, and chars organic substances. The liquid saturated with fluoboric gas, gives off when boiled, only one-fifth of the gas undecomposed: after that, its boiling point rises far above 100°, and it may then be distilled without decomposition.

Decomposition. By dilution with water, into hydrofluoboric acid and boracic acid, the latter separating in the solid form.

Combinations.—*α.* With sulphuric acid.—*β.* With hydrofluates of metallic oxides. (Vid. *Metallic Fluorides.*)

b. Hydrofluoboric Acid. $BO^3,4HF$.

1. When fluoboric gas or aqueous solution of fluoboric acid comes in contact with a considerable quantity of water, one-fourth of the boracic acid is set at liberty, and separates, sometimes in gelatinous flakes, sometimes as a crystalline powder, while hydrofluoboric acid remains in the liquid.

$$4(BO^3, 3HF) = 3(BO^3, 4HF) + BO^3;$$

or, if it be supposed that 1 atom of boracic acid is replaced in the liquid by 3 atoms of water:

$$4(BO^3, 3HF) + 3HO = 3(BO^3, 3HF + HO, HF) + BO^3;$$

according to the latter view, hydrofluoboric acid is a compound of fluoboric acid, with a hydrate of hydrofluoric acid, $= BO^3,3HF + HO,HF$; and corresponds to those salts of fluoboric acid in which an atom of water is replaced by an atom of a metallic oxide.—2. The same liquid is obtained by dissolving crystallized boracic acid in dilute hydrofluoric acid, adding the boracic acid in small quantities at a time, till the liquid is saturated, and decanting the solution from the excess of boracic acid. (Berzelius.)

If the liquid is left to evaporate spontaneously, hydrofluoric acid escapes and fluoboric acid remains; if it be left to evaporate in contact with boracic acid, the hydrofluoric acid takes up more boracic acid, as the quantity of water diminishes, and at length the whole is converted into fluoboric acid. (Berzelius.)

¶ Berzelius supposes that when fluoboric gas is passed through water, in quantity sufficient to render it strongly acid, but not to saturate it, an interchange of elements takes place between the water and a portion of the fluoride of boron, whereby hydrofluoric acid and boracic acid are formed, and the hydrofluoric acid combines with the undecomposed fluoride of boron: thus,

$$4BF^3 + 3HO = BO^3 + 3(BF^3, HF).$$

The compound BF^3,HF is not known in the separate state, but is obtained in the form of aqueous solution, by either of the processes above mentioned ($BO^3, 4HF = BF^3, HF + 3HO$). When it comes in contact with a salifiable base, its hydrogen is oxidated at the expense of that base, and the radical of the base combines with the fluorine: the result is a compound of a metallic fluoride with fluoride of boron: thus, with potassa: $BF^3,HF + KO = BF^3,KF + HO$. (Berzelius, *Traité*, I., 765.) ¶

Fluorine and Phosphorus.

Fluoride of Phosphorus.—First obtained by Sir H. Davy, by distilling phosphorus with fluoride of lead or fluoride of mercury, a phosphide of the metal being left behind. Prepared by distilling fluoride of lead with phosphorus. Colourless, strongly fuming liquid, corresponding to terchloride of phosphorus. (Dumas, *Ann. Chim. Phys.* 31, 435.)

Fluorine and Sulphur.

A. Fluoride of Sulphur.—By distilling fluoride of lead or fluoride of mercury with sulphur. (H. Davy, Dumas.)

B. Sulphate of Fluoride of Boron.—Oil of vitriol of specific gravity 1·850 absorbs 50 times its volume of fluoboric gas. The same

compound is also obtained as a distillate towards the end of the operation for preparing fluoride of boron. Very viscid, fuming mixture, more volatile than pure oil of vitriol. When it is mixed with water, a very dense, white precipitate is formed. (J. Davy.)

Fluorine and Selenium.

Fluoride of Selenium.—Vapour of selenium passed over fluoride of lead kept in a state of fusion in a platinum crucible, produces fluoride of selenium, which condenses in crystals in the receiver. These crystals may be volatilized without decomposition at a high temperature; they dissolve in concentrated hydrofluoric acid, but are instantly decomposed by contact with water. (G. J. Knox.)

Other Compounds of Fluorine.

With the metals, fluorine forms the *Metallic Fluorides* or *Hypothetically anhydrous Fluates* (*Fluorures, Fluates secs*). These compounds are formed—1. When hydrofluoric acid is brought in contact with various metallic oxides, hydrogen gas being also disengaged.—2. By bringing hydrofluoric acid in contact with metallic oxides—whereby, either a solid metallic fluoride is formed directly, or a hydrated metallic fluoride or hydrofluate is produced, and subsequently decomposed by heat into water and a solid metallic fluoride.—3. By heating electro-negative metals with fluoride of lead or fluoride of mercury.—4. When the metallic fluoride to be formed is volatile, it may be formed by heating fluor-spar with the metallic oxide and oil of vitriol. The metallic oxide gives up its oxygen to the calcium, which remains in the form of sulphate of lime, and the fluorine combines with the metal, forming a metallic fluoride which distils over. The fluorides have no metallic lustre; one of them, the fluoride of silicium, is gaseous; most of them are easibly fusible, and for the most part resemble the metallic chlorides. They are not decomposed by ignition, either alone or mixed with charcoal. When ignited in the air, in a flame which contains aqueous vapour, many of them, as fluoride of calcium and cryolite, take up oxygen and are converted into metallic oxides, while the fluorine is given off in the form of hydrofluoric acid. (Smithson, *Ann. Phil.* 23, 100.) Chlorine decomposes the fluorides of potassium, sodium, mercury, and silver, converting them into chlorides, (Sir H. Davy.) Metallic fluorides are not decomposed by ignition with glacial phosphoric acid, unless silica is also present (the latter then gives up its oxygen to the metal, while the silicium escapes in combination with the fluorine) (Gay-Lussac & Thénard.) Vapour of anhydrous sulphuric acid passed over fluoride of calcium or any other metallic fluoride ignited in a platinum tube, does not effect the slightest decomposition. Hydrochloric acid gas, under these circumstances, liberates hydrofluoric acid. (Kuhlmann, *Pogg.* 10, 618.) Aqueous sulphuric and nitric acid decompose most metallic fluorides, yielding a sulphate or a nitrate and hydrofluoric acid. Oil of vitriol dissolves many metallic fluorides at ordinary temperatures, forming a thick, tenacious liquid which evolves hydrofluoric acid when heated. When a metallic fluoride is gently heated with oil of vitriol in a platinum crucible—the crucible covered with a glass plate on which a difficultly fusible etching ground has been laid—lines traced out upon it—the plate removed after a while—and the etching ground

cleaned off,—the lines are found to be bitten in, and appear particularly distinct when breathed upon. If the aqueous solution of a metallic fluoride be mixed with sulphuric acid, and the mixture left to dry on a glass plate similarly waxed and etched, the lines on the plate are likewise rendered opaque. If the metallic fluoride is very small in quantity or contaminated with silica, the mixture with sulphuric acid should be left to evaporate on a watch-glass—which would not be attacked by sulphuric acid alone—and the residue washed off with water; the spot on which the mixture has evaporated appears dull. (Berzelius.)

Hydrated Metallic Fluorides, Salts of Hydrofluoric acid, or *Hydrofluates* (*Hydrofluor-Salze, fluorwasserstoffsäure Salze, Hydrofluates, Fluorhydrates*).—These compounds are obtained;—1. By dissolving metallic fluorides in water. Some metallic fluorides dissolve readily in water (the fluorides of tin and silver); others sparingly (potassium, sodium, and iron); many are but very slightly soluble (the fluorides of strontium and cadmium); and many not at all (barium, calcium, magnesium, cerium, and yttrium).—2. By dissolving a metallic oxide in aqueous hydrofluoric acid (oxide of titanium, oxide of tantalum, and tungstic acid).—3. By dissolving various metals in aqueous hydrofluoric acid, the solution being attended with evolution of hydrogen gas (zirconium, tantalum, unignited silicium); or in a mixture of hydrofluoric acid and nitric acid (titanium, tantalum, ignited silicium). The solutions of the simple hydrofluates of ammonia, potash, and soda, have an alkaline reaction. The evaporation and cooling of the solution of a metallic fluoride yields hydrated crystals in some few cases; but more generally, an anhydrous fluoride. Solutions of metallic fluorides attack glass vessels in which they are evaporated or merely preserved. The aqueous solutions mixed with lime-salts give a precipitate of fluoride of calcium in the form of a transparent gelatinous mass, which is scarcely visible, because its refractive power is nearly the same as that of the liquid: the addition of ammonia makes it plainer. This precipitate, if it does not contain silica, dissolves with difficulty in hydrochloric or nitric acid, and is again precipitated by ammonia. From acetate of lead, the aqueous metallic fluorides generally precipitate fluoride of lead in a pulverulent form. They do not precipitate nitrate of silver.

Hydrofluates of Metallic Fluorides. Acid Metallic Fluorides of Berzelius.—Many metallic fluorides combine with one atom of hydrofluoric acid, forming compounds which are frequently crystalline. These compounds dissolve in water, forming solutions which redden litmus and may be regarded as solutions of bi-hydrofluates of metallic oxides.

$$KF, HF + HO = KO, 2HF.$$

Many metallic fluorides which are insoluble in water, such as the fluorides of barium and calcium, dissolve in aqueous hydrofluoric acid; and many which are sparingly soluble in water dissolve with greater facility in aqueous hydrofluoric acid. (Berzelius.)

Metallic Fluoborides. Many metallic fluorides combine with one atom of fluoride of boron. Thus, the double fluoride of boron and potassium is KF, BF^3. These compounds are obtained in solution:—1. By mixing an aqueous solution of fluoboric acid with a metallic fluoride.—2. By dissolving a metallic oxide in hydrofluoboric acid.

$$KO + BO^3, 4HF = KF + BF^3 + 4HO;$$

or, if we suppose that the solution contains a hydrofluate of the metallic oxide combined with hydrofluoboric acid, the mode of formation will be:

$$KO + BO^3, 4HF = KO, HF + BO^3, 3HF.$$

—3. By mixing the aqueous solution of the hydrofluate of a metallic oxide with boracic acid; under these circumstances, however, half the metal is set free in the form of oxide.

$$2(KF, HF) + BO^3 = KF, BF^3 + KO + 2HO;$$

or, on the assumption that the solution contains fluoborate of potassa:

$$2(KO, 2HF) + BO^3 = (KO, HF + BO^3, 3HF) + KO.$$

This liberation of the metallic oxide explains the phenomenon first observed by Zeise, (*Schw.* 32, 306,) viz. that the solution of bihydrofluate of ammonia, potassa, or soda, which has an acid reaction, becomes alkaline on the addition of boracic acid. When the solutions obtained by either of these methods are evaporated to the crystallizing point or to dryness, the anhydrous metallic fluoborides remain behind.

These compounds, when heated to redness, evolve fluoboric gas and are converted into metallic fluorides. When distilled with oil of vitriol, they yield gaseous fluoride of boron, together with liquid fluoboric acid, and excess of hydrofluoric acid, (which corrodes glass,) and leave a sulphate of the metallic oxide. (Berzelius.) Most of the metallic fluoborides dissolve in water either without alteration as fluoborides, or as fluoborates of metallic oxides—that is to say, as double salts, composed of 1 At. of mono-hydrofluate of a metallic oxide and 1 At. of terhydrofluate of boracic acid, (fluoboric acid,) the boracic acid, in fact, playing the part of one of the bases of the double salt. The solutions yield by evaporation either crystals of anhydrous metallic fluoboride or of the hydrated compound. (Berzelius.)

Fluoride of phosphorus and fluoride of sulphur likewise enter into combination with metallic fluorides, as with fluoride of sodium, &c. (Berzelius.)

Compounds of metallic Fluorides, one with the the other, *Metallic Fluorine salts.* The compounds of electro-negative metals with fluorine, such as bifluoride of silicium, bifluoride of platinum, sesquifluoride of aluminum, chromium, uranium or iron, &c., combine with the electro-positive metallic fluorides (as the fluorides of potassium, sodium, &c.) generally in equal numbers of atoms. The metallic fluorine-salts are sometimes obtained by directly mixing the two metallic fluorides dissolved in water, sometimes by bringing an electro-positive compound of hydrofluoric acid and a metallic fluoride (an alkaline bihydrofluate for example,) in contact with an electro-negative metallic oxide. Most metallic fluorine-salts dissolve in water less easily than the metallic fluorides which they contain. (Berzelius.) The aqueous solution may be supposed to contain a double hydrofluate:

$$NaF, SiF^2 + 3HO = NaO, HF + SiO^2, 2HF.$$

The reactions of hydrofluoric acid may also be explained upon the older theory—corresponding to that already given with regard to hydrochloric acid—according to which, the acid obtained from fluor-spar is regarded as a compound of water with an acid not yet obtained in the free state, and this again as a compound of oxygen with an unknown radical, *Fluorium* or *Fluoricum.* The atomic weight of fluorium may either be estimated at 2·7; in which case, 1 At. fluorium with 1 At. oxygen will form 1 At. (=10·7) hypothetically anhydrous fluoric acid

this in combination with 1 At. water, will form 1 At. (=19·6) hydrofluoric acid in the state described on p. 360; and the hypothetical substance, fluorine, which the chlorine theory supposes to exist, must be regarded as a compound of one atom of fluorium with two atoms of oxygen (=18·7). Or: we may, according to Berzelius's earlier theory, double the atomic weight of fluorium (=5·4); in which case it will require 2 atoms of oxygen to form 1 atom of the hypothetically anhydrous fluoric acid, which in combination with 2 atoms of water, produces 1 atom (=39·4) of hydrofluoric acid (p. 360). Gaseous fluoride of boron is a compound of hypothetically anhydrous fluoric acid with boracic acid; and the metallic fluorides, namely gaseous fluoride of silicium, fluor-spar, &c., are compounds of hypothetically anhydrous fluoric acid with metallic oxides. The reason why the anhydrous hydrofluates are not decomposed by anhydrous acids,—with the exception of boracic acid, which is capable of acting as a base to anhydrous fluoric acid,—as well as all other explanations connected with the subject, correspond exactly with those already given under Chlorine.

Chapter XII.

NITROGEN.

Compounds of Nitrogen and Oxygen.

Lavoisier. *Crell. Neueste Endeck.* 2, 125.
Cavendish. *Crell. Ann.* 1786, 1, 99.
Demian, Troostwyk, Lauwerenburg & Vrolik, *Nitrous Acid. Schw. J.* 7, 243,
Sir H. Davy. *Chemical and Philosophical Researches chiefly concerning Nitrous Oxide.* London 1800.
Berzelius. *Gilb.* 40, 162. *Gilb.* 46, 131.
Gay-Lussac. *Ann. Chim. Phys.* 1, 394; also *Gilb.* 58, 29; also *Schw.* 17, 236.
Dulong. *Ann. Chim. Phys.* 2, 317; also *Schw.* 18, 177; also *Gilb.* 58, 53.
Dalton. *Ann. Phil.* 9, 186. *Ann. Phil.* 10, 38 & 83; also *Gilb.* 58, 79.
W. Henry, on *Nitrous Oxide, Nitric Acid and Ammonia, Manchester Mem. New Ser.* Vol. 4; also *Ann. Phil.* 24, 299 & 334; also *Kastn. Arch.* 3, 223.
Pleischl. *Nitrous Oxide, Schw.* 38, 461.
Hess. Nitrous Acid. *Pogg.* 12, 257.
Peligot. *Binoxide of Nitrogen or Nitric Oxide. Ann. Chim. Phys.* 54, 17; also *J. Pharm.* 19, 644; also *Schw.* 69, 341; also *Ann. Pharm.* 9, 259. *Nitrous and Hyponitric Acid. Ann. Chim. Phys.* 77, 58 & 87; the latter also *J. pr. Chem.* 23, 124 & 504; also *Ann. Pharm.* 39, 327.
Fritzsche. *Nitrous and Hyponitrous Acid. J. pr. Chem.* 19, 179; 22, 14.
Kuhlmann. *Ann. Pharm.* 29, 272; 39, 319.

Millon. *Nitric Acid.* *J. Pharm.* 29, 179; also *Compt. rend.* 14, 904.

Sulphite of Nitric Oxide. H. Davy, *Researches*, 317.—Pelouze. *Ann. Chim. Phys.* 60, 151; also *Pogg.* 39, 181; also *Ann. Pharm.* 18, 240; also *J. pr. Chem.* 11, 92.

Sulphate of Nitric Oxide: Clement & Desormes. *Ann. Chim.* 59, 329; also *N. Gehl.* 4, 457.—Dalton. *New System*, 2, 200.—Sir H. Davy. *Elements.* 1, 249.—Döbereiner. *Schw.* 8, 239.—Berzelius. *Gilb.* 50, 388.—Gay-Lussac. *Ann. Chim. Phys.* 1, 394.—W. Henry. *Ann. Phil.* 27, 368; also *J. Pharm.* 13, 113; also *Kastn. Arch.* 8, 463; abstr. *Pogg.* 7, 135.—Gaultier de Claubry. *Ann. Chim. Phys.* 45, 284; also *Schw.* 63, 284; also *Pogg.* 20, 467.—Dana. *Phil. Mag. J.* 3, 115.—Bussy. *J. Pharm.* 16, 491; also *N. Tr.* 23, 2, 118; abstr. *Pogg.* 20, 174.—Thomson. *J. Pharm.* 22, 655.—De la Frevostaye. *Ann. Chim. Phys.* 73, 362; also *J. pr. Chem.* 21, 401; also *N. Br. Arch.* 24, 163.—H. Rose. *Pogg.* 47, 605.—A. Rose. *Pogg.* 50, 161.

Dumas. *Solid and Liquid Nitrous Oxide.* *J. Pharm.* 14, 411; abst. *Ann. Pharm.* 68, 224.

Kolbe. *Formation of Nitric Acid in Eudiometrical experiments.* *Ann. Pharm.* 59, 208.

Deville. *Anhydrous Nitric Acid.* *Compt. rend.* Feb. 17, 1849; also *Chem. Gaz.* April 2, 1849.

Atmospheric Air:

Lavoisier. *Crell. Ann.* 1788, 2, 426.—Berthollet. *Scher. J.* 1, 518.—Von Humboldt. *Scher. J.* 5, 88 & 146.—De Marty. *Scher. J.* 8, 57; abstr. *Gilb.* 19, 389.—De Marty. *N. Gehl.* 4, 146; also *Gilb.* 28, 422.—Humboldt & Gay-Lussac. *A. Gehl.* 5, 45; also *Gilb.* 20, 38.—Dalton. *Gilb.* 27, 369.—*Phil. Mag. J.* 12, 397.—Hildebrandt. *Schw.* 14, 265.—Saussure. *Ann. Chim. Phys.* 2, 199; also *Gilb.* 54, 217.—*Ann. Chim. Phys.* 3, 170.—*Bibl. Univ.* 44, 23 & 138; also *Pogg.* 19, 391; also *Schw.* 60, 17 and 129.—*Bibl. Univ.* 56, 130; also *J. pr. Chem.* 3, 136.—*N. Bibl. Univ.* 2, 170; also *Pogg.* 38, 171; also *Ann. Pharm.* 19, 51.—Brunner. *Pogg.* 20, 274; 24, 569; 31, 1.—*Ann. Chim. Phys.* 78, 305.—Boussingault. *Ann. Chim. Phys.* 57, 148; also *Pogg.* 36, 456; also *J. pr. Chem.* 3, 151.—Dumas & Boussingault. *Compt. rend.* 12, 1005; also *Ann. Chim. Phys.* 78, 257; abstr. *Pogg.* 53, 391.—Dumas. *Compt. rend.* 14, 379.—Leblanc. *Compt. rend.* 14, 862; also *N. Ann. Chim. Phys.* 5, 223. Regnault & Reiset. *Compt. rend.* 26, 4 and 155.

Ammonia:

C. L. Berthollet. *Crell. Ann.* 1791, 2, 169.

Am. Berthollet. *N. Gehl.* 7, 184; also *Gilb.* 30, 378.

Thénard. *Schw.* 7, 299; also *Gilb.* 46. 267.

Sir H. Davy. *N. Gehl.* 7, 632; also *Gilb.* 31, 161.—*Schw.* 1, 302 & 324; 3, 334; also *Gilb.* 35, 151; 36, 180; 37, 35.—*N. Gehl.* 9, 507; also *Gilb.* 33, 246.—*Schw.* 4, 209; also *Gilb.* 37, 155.

W. Henry. *Phil. Transact.* 1809, 2, 429; also *Gilb.* 36, 291.

Berzelius. *Gilb.* 36, 198; 37, 210; 38, 176; 46, 131.

Bischof. *Schw.* 42, 257; 45, 204.

Faraday. *Quart. J. of Sc.* 19, 16; also *Pogg.* 3, 455; also *Schw.* 44, 341; also *Kastn. Arch.* 5, 442; also *N. Tr.* 11, 1, 64.

Bineau. *Ann. Chim. Phys.* 67, 325; 75, 251; also *J. pr. Chem.* 15, 257; 19, 6.

Kane. Ammonia and Amidogen Compounds: *Pogg.* 42, 367.—Further: *Ann. Chim. Phys.* 72, 225 & 337.—Also *J. Pr. Chem.* 15, 276.—Further: *Phil. Mag. J.* 17, 20.

J. Davy. Carbonate of Ammonia. *N. Ed. Phil. J.* 16. 245.

H. Rose. Carbonate of Ammonia. *Pogg.* 46, 352.

H. Rose. Anhydrous Sulphite of Ammon. *Pogg.* 33, 235; 42, 415.

H. Rose. Anhydrous Sulphate of Ammon. *Pogg.* 32, 81; 47, 471; 49, 183.

Ammonio-chloride of Phosphorus. Sir H. Davy. *Gilb.* 39, 6.—H. Rose. *Pogg.* 24, 308; 28, 530.—Wöhler & Liebig. *Ann. Pharm.* 11, 139.

Ammonio-chloride of Sulphur. Dumas. *Ann. Chim. Phys.* 49, 206.—Gregory. *J. Pharm.* 21, 315; 22, 301.—H. Rose. *Pogg.* 24, 307; 52, 60.—Soubeiran. *Ann. Chim. Phys.* 67, 71; also *J. Pharm.* 24, 49.—Bineau. *Ann. Chim. Phys.* 70, 267.—Martens. *J. Chim. Med.* 13, 430.

Compounds of Ammonium with Metallic Iodides, Bromides, and Chlorides. Faraday. *Quart. J. of Sc.* 5, 74.—H. Rose. *Pogg.* 20, 154; 52, 57.—Persoz. *Ann. Chim. Phys.* 44, 315; also *N. Tr.* 23, 3, 105.—Rammelsberg. *Pogg.* 58, 151; 55, 237.

Compounds of Ammonia with Anhydrous Oxygen-salts. H. Rose. *Pogg.* 20, 147.

Phosphide of Nitrogen. H. Rose. *Pogg.* 28, 529.—Wöhler & Liebig. *Ann. Pharm.* 11, 139.

Compounds containing Phosphorus and Nitrogen. Gerhardt. *N. Ann. Chim. Phys.* 18, 188. Gladstone. *Qu. J. of Chem. Soc.* 2, 121.

Sulphide of Nitrogen. Gregory. *J. Pharm.* 21, 315.—Soubeiran. *Ann. Chim. Phys.* 67, 71; also *J. Pharm.* 24, 71; also *Ann. Pharm.* 28, 59; also *J. pr. Chem.* 13, 449.

Iodide of Nitrogen. Serullas. *Ann. Chim. Phys.* 42, 200; also *Schw.* 58, 228; also *Pogg.* 17, 304.—Millon. *Ann. Chim. Phys.* 69, 78; also *J. pr. Chem.* 17, 1.—Marchand. *J. pr. Chem.* 19, 1.

Bromide of Nitrogen. Millon. *Ann. Chim. Phys.* 69, 75.

Chloride of Nitrogen. Dulong. *Schw.* 8, 302; also *Gilb.* 47, 43.—Porret, Wilson & Kirk. *Gilb.* 47, 56 and 69.—Sir H. Davy. *Phil. Transact.* 1813, 1 and 242; also *Gilb.* 47, 51.—Serullas. *Ann. Chim. Phys.* 69, 75; also *Schw.* 58, 224; also *Pogg.* 17, 304.—Millon. *Ann. Chim. Phys.* 69, 75.

Metallic Nitrides. Thénard. *Ann. Chim.* 85, 61; also *Gilb.* 46, 267.—Savart. *Ann. Chim. Phys.* 37, 326; also *Pogg.* 13, 172; also *N. Tr.* 18, 1, 295.—Despretz. *Ann. Chim. Phys.* 42, 122; also *Schw.* 58, 218; also *Pogg.* 17, 296; also *N. Tr.* 21, 1, 138.—Pfaff. *Pogg.* 42, 164.—Grove. *Phil. Mag. J.* 18, 548; 19, 97; also *Pogg.* 53, 363; 54, 107.—Schrötter. *Ann. Pharm.* 37, 128.—Plantamour. *N. Bibl. Univ.* 32, 339; also *Ann. Pharm.* 40, 115; also *J. pr. Chem.* 24, 220.

Stickstoff, Salpeterstoff, Azote, Nitrogène, Alcaligène, Septone, Azotum, Nitrogenium.—Nitrogen gas, Stickgas, Stickstoffgas, Salpeterstoffgas, Stickluft, phlogistisirte, verdorbene luft, Gas azote, Mofette atmosphèrique, Air vicié.

History. It has been known from very early times that the air is vitiated by the processes of combustion and respiration, and rendered

unfit for their further continuance. As long as the air was considered a simple substance, this fact was explained on the supposition that phlogiston was imparted to it by the burning body. Rutherford, in 1772, showed that in the process of respiration the air is by no means simply converted into carbonic acid, but that at the same time, an irrespirable air of a peculiar nature is left behind. Before 1777, Scheele separated the oxygen of the air from the nitrogen; he likewise discovered, almost simultaneously with Lavoisier, that the atmosphere is a mixture of these two gases.

From the nitrates, a class of substances known from very early times—and more particularly from saltpetre—the Arabians first, and afterwards the alchemists appear to have obtained aqueous *Nitric acid* (chiefly by heating a mixture of saltpetre with clay, till Glauber replaced the latter by sulphuric acid). Priestley very early remarked that a mixture of oxygen and nitrogen gases contracts and yields an acid when electrified; Cavendish, however, in 1785, first proved that the two gases unite completely and produce nitric acid. *Hyponitric acid* was first noticed by Scheele in 1774, and afterwards examined more particularly by Priestley, Berthollet, Davy, Thomson, Dalton, Berzelius, Gay-Lussac, and Dulong, the three latter chemists distinguishing from this acid the *Nitrous acid* hitherto confounded with it. *Nitrous gas* was first obtained by Hales, and afterwards more particularly examined by Priestley, Fontana, Humboldt, Davy, Dalton, Gay-Lussac, and others. Priestley, in 1776, discovered *Nitrous oxide gas*, which was examinedi n 1785 by Berthollet, in 1793 by the Dutch chemists, who investigated its composition, in 1800 by Sir H. Davy, and in 1823 by W. Henry and Pleischl.

The preparation of *Sal-ammoniac* was known even to the ancient Egyptians. *Carbonate of ammonia*, which is evolved either on heating sal-ammoniac with carbonate of lime, or from animal substances exposed to heat, appears to have been known to the Arabians. The alchemists were acquainted with *Solution of Caustic Ammonia*. Priestley discovered *Ammoniacal gas*, and observed its decomposition by electricity and by metallic oxides; Scheele showed that it is composed of nitrogen and phlogiston, by which name hydrogen is to be understood—as was subsequently proved by C. L. Berthollet, who, in concert with Am. Berthollet and W. Henry, determined more particularly the proportions in which the elements of this substance are combined. The compound of ammonia with phosphorus was examined in 1800 by Böckmann and A. Vogel; its compounds with phosgene and with chloride of boron, by J. Davy: with chloride of phosphorus, by Sir H. Davy and H. Rose; with chloride of sulphur, by Thomson, Dumas, Gregory, Soubeiran, Bineau; with oxychlorosulphide of carbon, by Berzelius; with metallic chlorides, by Faraday, Persoz, and H. Rose; and with anhydrous oxygen salts, by H. Rose.

Phosphide of Nitrogen was discovered and examined in 1833 by H. Rose; *Sulphide of nitrogen*, in 1835, by Gregory, and more accurately, in 1838, by Soubeiran; *Iodide of nitrogen*, in 1811, by Courtois; *Bromide of nitrogen*, in 1838, by Millon; *Chloride of nitrogen*, in 1812, by Dulong, who lost an eye in the investigation. The existence of *Metallic Nitrides* was proved especially by Savart, Despretz, Pfaff, Schrötter, and Plantamour.

Sources. As nitrogen gas, constituting 0·79 of the volume of the atmosphere; also in the air-bladders of fish, and in other cavities in the

bodies of animals and vegetables; in the salts of nitric acid, and of ammonia; in a vast number of organic compounds, especially in those belonging to the animal kingdom.

Preparation.—1. A portion of the oxygen contained in a confined portion of atmospheric air is removed by the slow or rapid combustion of phosphorus; by moistened alkaline sulphides or their aqueous solutions; by a mixture of iron filings and sulphur moistened with water; by prolonged agitation with a liquid amalgam of lead; by moistened charcoal; by excess of nitric oxide gas, the remaining portion of which is afterwards removed by agitation with solution of green vitriol; or by some other substance, which forms a liquid or solid gaseous compound with oxygen,—the carbonic acid gas being lastly absorbed by a caustic alkali. Dumas & Boussingault (*Compt. rend.* 12, 1005) pass atmospheric air, freed from carbonic acid by caustic potash and from aqueous vapour by oil of vitriol, over red-hot finely divided copper obtained by reducing oxide of copper with hydrogen gas. Brunner (*Pogg.* 27, 4) passes air thoroughly dried by means of chloride of calcium over red-hot finely divided iron (reduced from the sesqui-oxide by a current of hydrogen gas); a trace of moisture may in this case cause the nitrogen to be contaminated with hydrogen gas.—2. By decomposing ammonia with chlorine (*Sch.* 22); either by passing chlorine gas into solution of ammonia, or by introducing fragments of sal-ammoniac into a solution of chloride of lime.—3. By decomposing ammonia with an oxygen-compound of nitrogen. Pelouze (*Ann. Chim. Phys.* 77, 49) saturates oil of vitriol with nitric oxide gas, then adds sulphate of ammonia, and heats to a temperature of 160° (230° F.): in this manner, very pure nitrogen gas is obtained Emmet (*Lill. Ann. J.* 18, 259; also *Ann. Pharm.* 18, 168) heats nitrate of ammonia in a retort till it fuses; then, having attached a piece of zinc to a wire, introduces it into the fused salt to such a depth as to cause a moderately rapid disengagement of nitrogen. If the zinc were completely immersed, the action would be too violent. ¶ Carenwinder (*N. Ann. Chim. Phys.* 26, 296) heats a solution of nitrite of potash mixed with sal-ammoniac:

$$KO,NO^3 + NH^3,HCl = KCl + 4HO + 2N.$$

The solution of nitrite of potash is prepared by passing the nitrous gas evolved by heating 1 part of starch with 10 parts of nitric acid into a solution of caustic potash of specific gravity 1·38, till the liquid becomes decidedly acid, and then adding a sufficient quantity of caustic potash to restore the alkaline reaction. The solution of nitrite of potash thus obtained may be preserved without alteration. On mixing this liquid with 3 times its bulk of concentrated solution of sal-ammoniac, and gently heating the mixture in a small flask, nitrogen gas is evolved in abundance and with great regularity. The gas thus obtained is *perfectly pure.* The same result may be obtained by heating a solution of nitrite of ammonia: but that salt is difficult to prepare. ¶—4. By heating animal substances, such as muscle, in dilute nitric acid to a temperature of 30° (86° F.) and removing the nitric oxide disingaged at the same time, by means of a solution of green vitriol.

Properties. Colourless gas. (For the specific gravity and refractive power, *vid.* I., 280 and 95). Incombustible, and incapable of sustaining the combustion of other bodies; destitute of odour, taste, or action on vegetable colours. It may be breathed for a time, but does not support respiration; it is only negatively hurtful.

Combinations. Nitrogen manifests but few and very feeble affinities, whether towards highly electro-positive elements as hydrogen, or towards highly electro-negative elements as oxygen and chlorine. On the contrary, it has probably the greatest affinity of all ponderable bodies, for heat, with which it constantly tends to form a gas. Consequently many of its compounds are decomposed by slight causes, with extreme suddenness, the nitrogen being disengaged in the gaseous form, and often producing the most violent explosions.

Atomic weight of nitrogen, according to Berzelius = 7·09 (or 14·18), according to Dumas. (*Compt. rend.* 14, 546) = 7 (or 14.)

Nitrogen and Water.

Water at a temperature of 18° (64·4° F.) absorbs, according to Th. Saussure $\frac{1}{24}$; according to Dalton, $\frac{1}{64}$ of its volume of nitrogen gas.

Nitrogen and Oxygen.

Combination takes place very slowly, under peculiar circumstances only, and without perceptible disengagement of light or heat.

A. Nitrous Oxide. NO.

Protoxide of Nitrogen, Stickstoffoxydul, Protoxyde d'Azote, Oxyde nitreux, Oxydirtes Stickgas, Oxydulirtes Salpeterstoffgas, Dephlogistisirtes Salpetergas, Laughing gas, Wonnegas, Gas oxyde d'azote, Gas protoxyde d'azote.

Formation. This compound cannot be formed by the direct mixture of nitrogen and oxygen, but is produced by the decomposition of the higher oxygen compounds of nitrogen: for instance, on mixing nitric oxide gas with hydro-sulphuric acid, dry or moist liver of sulphur, moistened iron or zinc filings, hydrated protosulphide of iron (or hydrosulphate of ferrous oxide) salts of sulphurous acid in solution, or protochloride of tin; by heating nitrate of ammonia, (*Scheme* 72); and by dissolving zinc, tin, or iron in dilute nitric acid. (*Scheme* 25.) Copper treated with nitric acid of specific gravity 1·217, also yields nitrous oxide gas mixed with a small quantity of nitric oxide, provided the temperature be kept below —10°. (Millon.)

Preparation.—1. *In the gaseous form: a.* Neutral nitrate of ammonia free from hydrochloric acid, is heated in a glass retort (*App.* 34) to a temperature between 170° and 260° (338°—500° F.) One pound of nitrate of ammonia yields 4 cubic feet of gas. If too strong a heat be applied, a violent explosion may take place. At a higher temperature than the above, nitric oxide gas is also given off, and must then be separated by a solution of green vitriol. If chloride of ammonium is present in the nitrate, chlorine gas is disengaged, and must be removed by caustic potash. Grouvelle's method (*Ann. Chim. Phys.* 17, 351; also *Schw.* 33, 236), which consists in heating a mixture of 3 parts of nitrate of potash with 1 part of chloride of ammonium, instead of nitrate of ammonia, yields a gaseous mixture of chlorine, nitrogen, and nitric oxide, which, according

to Pleischl, contains a small quantity of nitrous oxide, but according to Soubeiran (*J. Pharm.* 13, 321; also *Pogg.* 13, 282), not even a trace.

b. By dissolving zinc in very dilute nitric acid. According to Grotthuss (*Schw.* 32, 271) and Pleischl, a perfectly pure gas is obtained in this manner; according to the latter, the best mixture for the purpose is 1 part of acid of specific gravity 1·2, with an equal weight or more of water; with a stronger acid, greater heat is evolved during the solution, and the nitrous oxide gas becomes contaminated with nitric oxide.

The gas is received over water, or brine (which absorbs less of it), or over mercury.

2. *In the liquid state.* *a.* Perfectly dry nitrate of ammonia placed at one end of a bent glass tube hermetically sealed, is heated till the whole has distilled over into the cold end; then this end is heated; and so on two or three times, till the greater portion of the salt is decomposed. In the cooler end, two strata of liquid condense, the lower of which is water containing nitrous acid and nitrous oxide in solution; the upper, liquid nitrous oxide. The apparatus is very liable to burst with extreme violence, so that the greatest caution is required in using it. (Faraday.) Niemann (*Pr. Arch.* 36, 177) did not succeed in this experiment. If the heat is applied till the manometer indicates a pressure of 75 atmospheres, water alone passes over; at a temperature above the melting point of lead, the pressure increases to 90 atmospheres, or water alone passes over, the greater part of the nitrate of ammonia, which, under this powerful pressure, is less readily decomposed by heat, remaining in the heated branch of the tube; on still further increasing the heat, explosion ensues.—*b.* By mechanical compression of the gas. (Natterer, *Pogg.* 12, 132.)

¶ 3. *In the solid state.* *a.* By exposing liquid nitrous oxide to the cold produced by the carbonic acid bath in vacuo (I., 287), the freezing point being about −100° C. or −150° F. (Faraday.)—*b.* When liquid nitrous oxide is allowed to escape into the air by opening the stop-cock of the vessel in which it has been condensed, the first portion which escapes is reduced to the solid state. (Dumas.)

Properties.—1. *In the solid state.* White, snow-like mass, which when placed on the hand, melts, evaporates suddenly, and produces a blister like a burn. (Dumas, *J. Pharm,* 14, 411.) Mixed with bisulphide of carbon in vacuo, it depresses the thermometer to −140° C. or −240° F. (Natterer. *Ann. Pharm.* 54, 254.)

2. *In the liquid state.* Colourless, very mobile; a single drop of it placed on the hand, produces a wound like a burn. Metals dipped into this liquid produce a hissing noise, just as when red-hot iron is plunged in water. Potassium swims on its surface without alteration: so likewise do charcoal, sulphur, phosphorus, and iodine. Ignited charcoal swims on the surface and burns with vivid light. The liquid is miscible with ether and alcohol. Sulphuric and nitric acid are immediately frozen by contact with it. Water also freezes, but at the same time causes the liquid nitrous oxide to evaporate with a degree of rapidity almost amounting to explosion. (Dumas.) ¶ Refracting power, less than that of any other liquid. (Faraday.)

3. *In the gaseous state.* Colourless gas. [Tension, specific gravity and refractive power, I., 261, 280, and 95.] It has a slight, agreeable odour, and a sweet, pleasant taste. It may be respired for a short time, not exceeding four minutes, and then produces very remarkable effects,

mostly of an intoxicating character. Wedgewood, Sir H. Davy, and others, were agreeably affected by it, experiencing great hilarity and intoxication, and ultimately loss of consciousness: these symptoms were followed by exhaustion. With Thénard, paleness and loss of strength ensued, even to fainting. Vauquelin experienced very disagreeable, suffocating sensations; Proust, confusion of sight, double vision, anxiety, fainting, and unpleasant sensations; Cardone (*J. Chim. Med.* 2. 132), violent pain in the temples, which lasted for an hour; confused sight with double vision; indistinct hearing, amounting at intervals to deafness; violent perspiration over the whole body; a soapy taste in the mouth at first, afterwards sweet, and lastly acid, with dryness in the throat, great inclination to talk and laugh, and finally, melancholy and drowsiness; after which the effects ceased. In the case of one person, it even produced delirium, with violent movements similar to the St. Vitus' dance, which continued for several days (*Schw.* 36, 244). Animals, when immersed in the gas, becomes restless after a while, and die after a longer interval.

The gas is not combustible: a candle introduced into it, burns with greater brilliancy than in the air: a glowing match introduced into a jar of the gas bursts into flame. When mixed with nitric oxide gas, it neither produces red vapours, nor suffers diminution of volume. It has no effect on vegetable colours.

	Calculation.		H. Davy.	Deiman.
N	14	63·6	63·3	62·5
O	8	36·4	36·3	77·5
NO	22	100·0	100·0	100·0

	Vol.	Sp. gr.
Nitrogen gas	1	0·9706
Oxygen gas	½	0·5546
Nitrous oxide gas	1	1·5252

($N^2O = 2 . 88·52 + 100 = 277·04$. Berzelius.)

Decompositions.—1. By long continued electrization, or when passed through an ignited porcelain tube, nitrous oxide gas is resolved—with diminution of volume amounting to about 0·1, and production of a small quantity of hyponitric acid—into a mixture of oxygen and nitrogen gases. (Priestley.)

2. When mixed with one volume of hydrogen gas and exploded by the electric spark, or when passed through a red hot tube, one volume of nitrous oxide is converted into water and one volume of nitrogen gas; with a smaller quantity of hydrogen, nitric acid is also produced. (Priestley, Sir H. Davy, W. Henry.) Spongy platinum becomes ignited in the above mixture, and converts it into water and nitrogen gas. (Döbereiner, Dulong & Thénard.) When excess of hydrogen is present, ammonia is also formed. (Kuhlmann.) (Vid. *Ammonia.*) Nitrous oxide gas likewise explodes by the electric spark, or at a red heat, when mixed with ammoniacal gas or with carburetted, phosphuretted, or sulphuretted hydrogen, yielding nitrogen gas, water, and carbonic, phosphorous, or sulphurous acid. Spontaneously inflammable phosphuretted hydrogen gas explodes with nitrous oxide, even at ordinary temperatures (Thénard); according to Berzelius, however, the mixture does not explode tillit is exposed to the air, whereby the phosphuretted hydrogen is set on fire, or till an electric spark is passed through it. A mixture of 1 volume of phosphuretted hydrogen gas with 3 volumes of nitrous oxide yields water, phosphoric acid, and 3 volumes of nitrogen gas. (Thomson.) The mixture explodes with great violence when the electric spark is passed through it; and if the nitrous oxide is in excess, 4 volumes of phosphuretted hydrogen gas are decomposed with 21 volumes of nitrous oxide gas, 3 volumes of oxygen combining with the hydrogen, and 7·5 volumes with the phosphorus in

the phosphuretted hydrogen gas. (Dumas.) If we assume with H. Rose that 4 volumes of phosphuretted hydrogen gas contain 1 volume of vapour of phosphorus and 6 volumes of hydrogen gas, then 5 volumes of oxygen will combine with the phosphorus, and 3 volumes with the hydrogen, so that 4 volumes of phosphuretted hydrogen gas will require 8 volumes of oxygen gas, contained in 16 volumes of nitrous oxide gas.—3. A mixture of 1 volume of carbonic oxide gas with rather more than 1 volume of nitrous oxide, yields, when exploded by the electric spark, 1 volume of carbonic acid, rather more than 1 volume of nitrogen, and a small quantity of free oxygen, because the excess of nitrous oxide is resolved by the heat into its gaseous elements. (W. Henry.)

4. Ignited charcoal burns in nitrous oxide more vividly than in common air, 1 volume of the gas being converted into 1 volume of nitrogen gas and a half volume of carbonic acid gas. (Sir H. Davy.) Heated boron burns in the gas, forming boracic acid and separating the nitrogen. Phosphorus may be volatilized in an atmosphere of the gas, or even touched with a red hot iron, without being inflamed; but if touched with a white hot iron or first set on fire in the air and then introduced into the gas, it burns almost as vividly as in oxygen gas, though for a shorter time, and produces phosphoric acid, with separation of nitrogen gas and formation of a small quantity of hyponitric acid. (H. Davy.) Sulphur brought into a state of feeble combustion in the air, is extinguished by immersion in nitrous oxide; when in full combustion, however, it continues to burn with a rose-coloured flame, and is converted into sulphurous acid. (Davy.) Boron, phosphorus, and sulphur, under these circumstances, liberate 1 measure of nitrogen for each measure of nitrous oxide.

5. Potassium and sodium, gently heated in nitrous oxide, burn at first with violent incandescence, and form peroxides, which, when further heated, decompose the gas, and are converted into salts of nitrous acid, while nitrogen and nitric oxide gases remain behind. (Gay-Lussac & Thénard.)—6. An intensely heated steel spring burns in this gas almost as brilliantly as in oxygen (Priestley); similarly, manganese, zinc and tin, in a state of ignition are oxidized in the gas, a volume of nitrogen being separated, equal to that of the nitrous oxide (H. Davy.)

Fuming nitric acid introduced into the gas diminishes its volume, in a manner not yet explained. (Demian, *Scher. J.* 7, 260.)

Hypochlorous acid gas does not affect it at ordinary temperatures. (Balard.) Salts of ferrous or stannous oxide, salts of hydrosulphuric and sulphurous acid, and nitric oxide gas, do not separate oxygen from nitrous oxide.

Combinations.—*a.* One volume of water at ordinary temperatures absorbs, according to W. Henry, from 0·78 to 0·16; according to Dalton, 0·80; according to Th. Saussure, 0·76; according to Sir H. Davy, 0·54; and according to Pleischl, at a temperature of 18°, 0·708 vol. of nitrous oxide gas; the solution has a sweetish taste. At a boiling heat, the gas is evolved unchanged. (Priestley.)

It is not absorbed by aqueous solutions of ferrous salts.

b. Nitrous oxide is absorbed by alcohol or ether, and by oils either fixed or volatile.

B. Nitric Oxide. NO^2.

Bioxide of Nitrogen, Binoxide of Nitrogen, Deutoxide of Nitrogen, Stickstoffoxyd, Oxyde nitric, Oxyde d'Azote, Deutoxyde d'Azote, Bi-oxyde d'Azote.—Nitric oxide gas, Stickoxyd-gas, Salpetergas, Oxydirtes, Salpeterstoffgas, Nitrous air, Nitrose Luft, Gas nitreux, Gas deutoxyde d'Azote, Gas nitrosum.

Formation.—1. When ammoniacal gas is passed over peroxide of manganese or calcined green vitriol heated to redness in a gun-barrel. (Milner, *Crell. Ann.* 1, 7951, 554.)—2. When nitrous, hyponitric, or nitric acid, is brought in contact at a temperature below redness with charcoal, phosphorus, sulphur, organic substances, and with various metals.

Preparation. By dissolving copper (*Sch.* 24), bismuth, lead, silver, or mercury in nitric acid of specific gravity from 1·2 to 1·3. The more dilute the acid, and the lower the temperature at which it acts, the less is the gas contaminated with free nitrogen. Copper treated with dilute acid,—if the rise of temperature be prevented by a freezing mixture—yields the purest gas, perfectly absorbed by a solution of green vitriol. (Millon, *Compt. rend.* 14, 908.) The gas is received over water.

When concentrated nitric acid is heated with copper in a sealed bent tube,—a blackish green stratum of liquid, of specific gravity about 1·0 or 1·2 appears above the copper solution, as soon as the pressure amounts to 20 atmospheres. This liquid, when shaken, separates not into drops but into flakes, which however soon reunite; when gently heated it distils over into the cold empty branch of the tube and appears of a bluish green colour. If the pressure in the tube increases to more than 50 atmospheres, the liquid entirely disappears. Mercury cannot be used instead of copper in this case, because the mercurial solution absorbs the nitric oxide gas, so that the pressure never rises above two atmospheres. (Niemann, *N. Br. Arch.* 4, 26.)

Properties. Colourless gas. (For its specific gravity and refractive power see I., 280 and 95.)—Inhaled in a pure state it destroys life. Does not redden litmus. Is not combustible. Supports the combustion of but few substances, not that of a candle for instance. Forms yellowish red vapours in the air. It is copiously absorbed by a solution of ferrous sulphate, forming a dark-brown coloured liquid. It imparts a red colour to oil of vitriol containing a small quantity of ferrous sulphate, and a violet colour to oil of vitriol containing sulphate of copper. (Desbassins de Richemont. *J. Chim. Med.* 11, 504.)

	Calculation.		H. Davy.	Lavoisier.	Dalton.	Berzelius.
N	14.	46·67	42·3	32.	42.	46·754
2O	16.	53·33	57·7	68.	58.	53·246
NO^2	30.	100·00	100·0	100.	100.	100·000

	Vol.	Sp. gr.		Vol.	Sp.gr.
Nitrogen gas	1	0·9706	=	½	0·4853
Oxygen gas	1	1·1093	=	½	0·5546
Nitric oxide gas	2	2·0799	=	1	1·0399

(NO = 88·52 + 100 = 188·52. Berzelius.)

Decompositions. 1. By a prolonged succession of electric sparks (Priestley), or by transmission through an ignited tube containing platinum wire, (Gay-Lussac), nitric oxide gas is resolved into nitrogen gas and hyponitric—or, if water be present—nitric, acid.—2. When kept for 3 months in contact with a concentrated solution of caustic potash, it is resolved into $\frac{1}{4}$ vol. of nitrous oxide gas, and nitrous acid, which latter combines with the potash. (Gay-Lussac.)

3. A mixture of 2 volumes of nitric oxide gas and 1 volume of sulphurous acid gas, placed over water for a few hours, condenses to aqueous sulphuric acid and 1 volume of nitrous oxide gas. (Pelouze, *Ann. Chim. Phys.* 60, 162.)

$$SO^2 + NO^2 = SO^3 + NO.$$

Moistened alkaline sulphites, protochloride of tin, and anhydrous sulphide of potassium reduce 2 volumes of nitric oxide gas, at ordinary temperatures, to 1 volume of gaseous nitrous oxide, by absorbing 1 atom of oxygen.—4. A mixture of equal volumes of hydrosulphuric acid and nitric oxide, is resolved in a few hours, into a small quantity of nitrous oxide gas and hydrosulphite of ammonia: according to Thomson, this effect is most quickly produced when the gases are dry. In a similar manner, solutions of alkaline hydrosulphates and hydrosulphites, also moistened iron (see Thomson, *Ann. Phil.* 15, 225) and zinc filings introduced into nitric oxide gas, give rise, in the course of a few days, to the formation of nitrous oxide gas and ammonia,—the hydrogen uniting partly with the oxygen of the nitric oxide to form water, and partly with the nitrogen, to form ammonia. Aqueous solutions of alkaline hydrosulphates convert nitric oxide gas into a mixture of nitrous oxide and nitrogen gases; a mixture of iron filings and sulphur moistened with water converts 100 measures of nitric oxide gas into 44 measures of pure nitrogen. (Berthollet, *Stat. Chim.* 2, 153 & 161.)

5. A mixture of nitric oxide and hydrogen (in equal volumes) explodes, according to Fourcroy and Thomson, when passed through a red-hot tube; according to Berthollet, however (*Stat. Chim.* 2, 145,) no explosion takes place; nor by the electric spark. (H. Davy.) The mixture, if set on fire in the air, does not explode but burns with a white (or, according to Berzelius, a green) flame, with formation of hyponitric acid vapour; hence it would appear that the hydrogen burns only at the expense of the atmospheric oxygen. An ignited jet of hydrogen gas thrown into an atmosphere of nitric oxide does not continue to burn. (Waldie, *Phil. Mag. J.* 13, 89.) According to Dulong & Thénard and Kuhlmann, cold spongy platinum converts the mixture into water and ammonia; but according to Döbereiner, no such effect takes place.

If a mixture of 2 measures of nitric oxide and 5 measures of hydrogen gas be passed in a fine stream through the neck of a small tubulated retort, directly upon spongy platinum contained in the retort, and the platinum be heated after all the air has been expelled, it will become red-hot and produce water and ammonia:

$$NO^2 + 5H = NH^3 + 2HO.$$

(Hare, *J. Pharm.* 24, 146,) (Vid. *Ammonia*). A prepared platinum plate (II., 47) introduced into a mixture of equal measures of the two gases at ordinary temperatures produces no condensation in the course of one hour; but in 36 hours, the condensation amounts to $\frac{1}{8}$ of the whole. (Faraday, *Pogg.* 33, 149.) A mixture of spontaneously inflammable phosphuretted hydrogen and nitric oxide is generally decomposed in a few

hours at ordinary temperatures, the residue consisting of nitrogen and nitrous oxide gases. (Dalton.) The mixture, when inflamed by the electric spark or by the admission of oxygen gas, explodes with a bright light, producing water and phosphoric acid and leaving free nitrogen. According to Thomson, 4 volumes of phosphuretted hydrogen gas mixed with excess of nitric oxide, decompose 12, or according to Dalton 14 volumes of the latter. Now if 4 volumes of phosphuretted hydrogen gas are assumed to contain 1 volume of phosphorus vapour and 6 volumes of hydrogen gas, they will together require $5+3=8$ volumes of oxygen, and will consequently decompose 16 volumes of nitric oxide. Ammoniacal gas may also be exploded with nitric oxide by the electric spark; according to Gay-Lussac, a mixture of the two gases slowly undergoes decomposition, at ordinary temperatures. [For the decomposition with *olefiant gas*, see the latter.]

6. Charcoal burns more brilliantly in nitric oxide gas than in common air. Nitric oxide passed over charcoal ignited in a tube is resolved into a half-volume of nitrogen gas and a half-volume of carbonic acid. (Dalton.) Pyrophori take fire in the gas and burn very vividly. (Sir H. Davy.) According to W. Henry, a mixture of carbonic oxide and nitric oxide gases—no matter in what proportions—cannot be inflamed by the electric spark. Phosphorus burning feebly is extinguished by nitric oxide; but if in full combustion, it continues to burn in the gas, almost with as much splendour as in oxygen, producing phosphoric acid and free nitrogen. Nitric oxide gas in which bi-sulphide of carbon is diffused, burns with a brilliant greenish coloured flame, when a lighted match is applied to it. (Berzelius.) Burning sulphur is extinguished in an atmosphere of nitric oxide.

7. Heated potassium burns vividly in nitric oxide gas: if the potassium is in excess, suboxide of potassium and nitrogen gas are the results; if the nitric oxide predominates, peroxide of potassium is first formed, and is afterwards converted, by further absorption of the gas, into nitrite of potash. Sodium, at the temperature of an ordinary lamp, has no action on nitric oxide. (Gay-Lussac & Thénard.) Red-hot iron, zinc, arsenic, and sulphide of barium absorb oxygen from nitric oxide, and separate half a volume of free nitrogen. (H. Davy; Gay-Lussac.)

Combinations.—*a.* One volume of water absorbs at ordinary temperatures, according to Sir H. Davy, $\frac{1}{10}$; according to W. Henry, $\frac{1}{20}$; and according to Dalton, $\frac{1}{27}$ vol. of nitric oxide gas.

b. With Sulphurous acid? *c.* With Sulphuric acid. *d.* With Flucride of Boron. *e.* With Fluoride of Silicium. *f.* With Bichloride of Tin. *g.* With ferrous salts in solution: these salts absorb the gas in great abundance, forming a dark brown liquid. (See also *Iron.*) Salts of stannous oxide also, according to Berzelius, absorb nitric oxide gas.

¶ According to Reinsch (*J. pr. Chem.* 28, 391; also *Buchn. Repert.* 32, 164), nitric oxide forms with several acids compounds analogous to that which it forms with sulphuric acid. With phosphoric acid, it forms a compound which crystallizes in fine four-sided prisms; with arsenic acid, a buttery mass which is decomposed by water; these compounds are obtained by passing the gas into a syrupy solution of the acid. It is also absorbed by a concentrated solution of tartaric acid. The crystallized hydrate of acetic acid forms a blue compound with it. When nitric oxide is passed into a bottle containing hydrochloric acid gas, an oily, yellowish

green liquid is produced, together with colourless crystals, which are instantly decomposed with effervescence by contact with water. The oily liquid immediately blackens solution of green vitriol. Both the liquid and the crystals decompose spontaneously after keeping for some days: chlorine gas is one of the products of the decomposition. ¶

C. Nitrous Acid. NO^3.

Hyponitrous acid, Salpetrige Säure, Untersalpetrige Säure, Acide pernitreux, Acide hyponitreux, Acide azoteux.

Formation.—1. By the decomposition of nitric oxide (p. 378).—2. When nitric oxide is mixed with one-fourth of its volume, or less, of oxygen gas. One volume of oxygen gas in contact with solution of potash and a very large excess of nitric oxide gas, condenses, at most, 4 volumes of the latter and produces nitrite of potash. (Gay-Lussac; see also Thomson, *Ann. Phil.* 17, 321.)—3. By passing nitric oxide gas through anhydrous hyponitric acid or concentrated nitric acid at ordinary temperatures:

$$NO^2 + NO^4 = 2NO^3;\ \text{and}\ 2NO^2 + NO^5 = 3NO^3.$$

With mercurous oxide also, nitric oxide produces mercurous nitrite. (Peligot.)—4. When hyponitric acid comes in contact with water or salifiable bases.—5. When nitrate of lead dissolved in water is boiled with metallic lead, the latter is oxidized at the expense of the nitric acid and produces a salt of nitrous acid. (Berzelius.)

Preparation.—1. 45 parts (5 atoms) of water are gradually poured through a glass tube drawn out to a fine point, into 92 parts (2 atoms) of hyponitric acid cooled down to a temperature of $-20°$ ($-4°$ F.); and the two green-coloured strata formed (*vid.* page 385) are heated in a retort, the receiver of which is surrounded by a freezing mixture, till the boiling point rises to 28° (82·4° F.). A distillate is obtained of an indigo-blue colour. (Fritzsche.)—2. A mixture of 1 volume of oxygen gas and rather more than 4 volumes of nitric oxide gas, is first passed through a tube filled with fragments of porcelain, to render the mixture more complete, and then into a curved tube cooled down to $-20°$; the acid collects in the lower portion of the latter in the form of a dark green liquid. (Dulong.)—3. Dry nitric oxide gas is passed through anhydrous hyponitric acid contained in a Liebig's potash-apparatus; a green liquid is then formed, the vapours evolved from which condense in a glass tube cooled down to a very low temperature, and form a bluish green, extremely volatile liquid, which may be regarded as a mixture of nitrous and hyponitric acids. (Peligot.)—4. One part of starch is heated with 8 parts of nitric acid of specific gravity 1·25; and the gaseous mixture disengaged is made to pass, first through a chloride of calcium tube two feet in length, and then into an empty glass tube cooled down to $-20°$, where it condenses to a very volatile liquid, which is colourless when exposed to extreme cold, but green at ordinary temperatures. (Liebig, *Geiger. Handb. d. Pharm. Anfl.* 5, 219.) By the partial distillation of the liquid obtained by Liebig's method, a dark green acid is obtained, which boils at $+10°$, but contains only 30·8 per cent. of oxygen; this liquid, if again partially distilled, yields an acid which boils at $-2°$, and contains 33 per cent. of oxygen; it is therefore still mixed with hypo-

nitric acid. (Peligot.) The green colour of the acid prepared by the second, third, and fourth methods indicates the presence of hyponitric acid; probably the first is the only method that yields a pure acid.

Properties. Nitrous acid, as obtained by the first method, is a deep indigo-blue coloured, highly volatile liquid, boiling below zero, probably even below − 10°. (Fritzsche.) Its vapour is yellowish red.

Calculation.				Vol.	or:	Vol.
N	14·	36·8	Nitrogen gas	2	Nitric oxide gas	4
3O	24·	63·2	Oxygen gas	3	Oxygen gas	1
NO^3	38·	100·0				

(N^2O^3 = 2 : 88·52 + 3 . 100 = 477·04. Berzelius.)

Decomposition. The acid prepared by the first method boils below zero; it then partly distils over undecomposed, and is partly resolved into nitric oxide gas and hyponitric acid, the latter remaining in the retort. (Fritzsche.)

$$2NO^3 = NO^2 + NO^4.$$

The nitrogen appears to have not much more affinity for the third atom of oxygen, than for the fourth, and for the latter not much more than for the fifth. Very trifling circumstances are therefore sufficient to alter the composition of the compounds of oxygen and nitrogen. The determining cause in the preceding case is the affinity of heat for the nitric oxide, or the elasticity of the latter; consequently nitrous acid can only exist, under the ordinary pressure of the atmosphere, at temperatures many degrees below 0°.

Combinations.—*a.* With water. The acid prepared by the first method dissolves in water at 0° abundantly and without decomposition, forming a light blue-coloured solution; at temperatures above 0°, however, the mixture evolves a large quantity of nitric oxide gas (Fritzsche), leaving a solution of nitric acid. (Mitscherlich.)

$$3NO^3 + n\,Aq = 2NO^2 + n\,Aq, NO^5.$$

In this case, the effect is produced by the affinity of heat for nitric oxide, and that of water for nitric acid. The aqueous acid, even when largely diluted, turns a solution of ferrous sulphate brown, by imparting nitric oxide to it.

b. With sulphuric acid?

c. With salifiable bases: *Salts of Nitrous acid, Nitrites, Azotites* (otherwise called *Hyponitrites*). 1. Nitric oxide gas is placed in contact with solution of caustic potash (see page 378).—2. A mixture of 1 volume of oxygen and 4 volumes of nitric oxide gas is passed through the aqueous solution of an alkali.—3. Liquid or gaseous hyponitric acid is brought in contact with salifiable bases dissolved or diffused in water. In this case, salts of nitrous and of nitric acid are formed at the same time; they may, however, be separated by their different degrees of solubility in water.

$$2KO + 2NO^4 = KO, NO^3 + KO, NO^5.$$

—4. Nitrate of potash or soda is heated till it gives up 2 atoms of oxygen,

$$NaO, NO^5 = NaO, NO^3 + 2O.$$

Mitscherlich (*Lehrb.* 1, 455) fuses nitrate of soda in an earthen crucible till a portion dissolved in water gives a brownish instead of a perfectly white precipitate, with nitrate of silver. (The white precipitate is

nitrite of silver; the brownish colour proceeds from a portion of the already produced nitrite of soda being decomposed and converted into caustic soda, which precipitates brown oxide of silver from the solution; (if the fusion is not carried thus far, a large quantity of nitrate of soda remains undecomposed.) He then dissolves the mass of salt in water: mixes it cold with nitrate of silver; collects the precipitated mixture of nitrite and free oxide of silver on a filter; dissolves out the former by boiling water; and sets it aside to crystallize. To obtain other nitrites from this salt, Mitscherlich decomposes it with an equivalent quantity of a metallic chloride,—for example:

$$AgO, NO^3 + KCl = KO, NO^3 + AgCl.$$

Fischer (*Pogg.* 21, 160), who employs nitrate of potash proceeds in a manner similar to the above.—5. An aqueous solution of nitrate of lead is boiled with metallic lead. (Berzelius.)

The salts of nitrous acid are either colourless or yellow, and for the most part crystallizable. The alkaline nitrites, according to Fischer, are neutral to vegetable colours; according to H. Rose, they are alkaline. They also fuse, when heated, forming a yellowish liquid which on cooling solidifies to a crystalline mass. When strongly heated, these salts evolve their acid in the form of nitrogen and oxygen gas. The aqueous solution of a nitrite is decomposed by long boiling into nitric oxide and a salt of nitric acid with excess of base. (Berzelius.)

$$3(KO, NO^3) = 2KO + KO, NO^5 + 2NO^2.$$

The nitrites detonate when heated with combustible bodies. When treated with oil of vitriol out of contact of air, they evolve nitric oxide gas, while the liquid takes up hyponitric and nitric acids. (Gay-Lussac.) If air be admitted, the free nitric oxide produces red fumes. Weaker acids, as acetic acid, also produce the same reaction. The nitrites precipitate the metals from solutions of chloride of gold and nitrate of mercurous oxide; from salts of manganous or ferrous oxide they throw down manganic or ferric oxide, and evolve nitric oxide gas. (Fischer.) With oil of vitriol to which a solution of ferrous sulphate has been added, they form a dark red liquid. When their aqueous solutions are boiled in open vessels, they readily absorb oxygen and are converted into nitrates. (Berzelius.) All the normal salts of nitrous acid are soluble in water, those of potash, lime, magnesia and protoxide of manganese being also deliquescent. Most of the other nitrites dissolve readily, with the exception of the nitrite of silver, which is but difficultly soluble; consequently, the other salts, when not too largely diluted, give a white precipitate with nitrate of silver. The alkaline nitrites form double salts with the nitrites of lead, cobalt, nickel, silver, and palladium. (Fischer.)

Deiman, Hess, and R. W. Fischer regard the above salts not as salts of nitrous acid (*e. g.* KO, NO^3) but as salts of nitric oxide (KO, NO^2).

D. HYPONITRIC ACID. NO^4.

Nitrous Acid, Salpetrige Säure, unvollkommene Salpetersäure, Acide nitreux, Acide hypoazotique.

Formation.—1. When oxygen and nitric oxide gases, in any proportions whatever, are mixed together at ordinary temperatures, and in the absence of water and salifiable bases, 2 volumes of nitric oxide invariably combine

with 1 volume of oxygen, to form 1 volume of hyponitric acid vapour. (Gay-Lussac.)—2. Hypochlorous acid gas explodes with nitric oxide gas at ordinary temperatures, producing hyponitric acid vapour and chlorine gas. (Balard.)

$$NO^2 + 2ClO = NO^4 + 2Cl.$$

—Euchlorine gas mixed with nitric oxide instantly forms red fumes. (H. Davy.)—3. Chlorine gas in the dry state does not act on nitric oxide; but if water is present, the chlorine takes up its hydrogen, and the nitric oxide, combining with the oxygen set free, is converted into hyponitric acid.—4. Hyponitric acid is produced in the decomposition (1) of nitrous oxide; in the decomposition (1) of nitric oxide; and in the decomposition of aqueous nitric acid and its salts by light, electricity, heat, and numerous deoxidizing substances, and especially in the transmission of nitric oxide gas through concentrated nitric acid.

Preparation.—1. A perfectly dry mixture of 1 volume of oxygen gas with nearly 2 volumes of nitric oxide is passed, first through a tube filled with pieces of porcelain, and then through a curved tube cooled down to a temperature of $-20°$, where the hyponitric acid vapour condenses, with separation of a small quantity of oxygen, to a greenish liquid (containing nitrous acid?), which however turns yellow even on decantation. (Dulong.) The gases cannot be rendered perfectly dry by chloride of calcium; they must, therefore, be passed in the required proportions, first over oil of vitriol, then through a tube filled with fragments of recently fused hydrate of potash, and lastly into a long-necked receiver cooled down to $-15°$ or $-20°$. If by this treatment all traces of water have been completely removed, the acid solidifies in colourless crystals. After the hydrate of potash has been used for some time, it ceases to dry the gases completely; and if the process is continued, the crystals deliquesce and form a green liquid, which, when any excess of oxygen is present, becomes continually darker and more volatile. (Peligot.) [At $-20°$, and with water present, nitrous acid appears to be the principal product in the above process, and mixes with the hyponitric acid in constantly increasing quantities.] To obtain hyponitric acid in the form of vapour, a mixture of two volumes of nitric oxide with one volume of oxygen is passed into a dry exhausted glass globe.—2. Perfectly dry nitrate of lead is heated in a retort connected with a cooled receiver, till it is completely decomposed. (Gay-Lussac.) The hyponitric acid collects in the receiver, while the excess of oxygen escapes by a tube fixed into the tubulure. According to Dulong, the acid thus obtained is anhydrous, or contains at most 0·006 water. To obtain the acid by this process perfectly anhydrous and crystallized, the nitrate of lead is dried till decomposition commences, and then distilled in a porcelain retort, the distilled product passing into a receiver which is kept at a very low temperature and changed during the operation. A greenish liquid containing water first passes over, then a colourless liquid containing a small quantity of water, and lastly the anhydrous acid which solidifies in crystals. (Peligot.)—3. When fuming nitric acid is gently heated in a retort connected with a receiver surrounded with a freezing mixture, two immiscible strata of liquid collect in the receiver. The lower of these is a mixture of hyponitric acid and mono-hydrated nitric acid; the upper, hyponitric acid containing a small quantity of mono-hydrated nitric acid. On distilling the latter at a gentle heat, the hyponitric acid passes over in a state of purity. (Mitscherlich, *Lehrb.* 1, 457.)

If the acid is required in crystals, it must be freed by partial distillation from the nitric acid mixed with it, [probably formed by the presence of a trace of water,] the receiver being cooled down to a temperature of $-20°$. (Fritzsche.)

Properties. Crystallizes at $-20°$ in colourless prisms (Peligot, Fritzsche); melts at $-9°$ (Peligot), at ($+$ or $-$?) $13.5°$ (Fritzsche). After being melted, the acid does not again solidify at $-16°$ (Peligot), the temperature required for that purpose being as low as $-30°$, because a trace of nitric acid has been formed: the same cause also gives rise to turbidity during the cooling of the liquid. (Fritzsche.)—In the liquid state, hyponitric acid has a specific gravity of 1·451 (Dulong); at a temperature of $-20°$, it is colourless; at $-10°$, almost colourless; between $0°$ and $+10°$, pale-yellow; from $+15°$ to $28°$, orange-yellow, the colour becoming darker as the temperature rises. (Dulong.) At $22°$ it boils, the thermometer remaining stationary (Peligot); at $26°$ (Gay-Lussac); at $28°$, with the barometer at 0·76 met. (Dulong.) It forms a dark yellowish red vapour which was formerly considered as a permanent gas, because when mixed with other gases it is not condensed by exposure to cold. It has a peculiar sweetish and pungent odour, and an acid taste. Its effects when inhaled are most injurious. It reddens litmus, and stains animal matter yellow.

	Calculation.		Dulong.	Peligot.
N	14·	30·44	29·96	30·57
4O	32·	69·56	70·04	69·43
NO^4	46·	100·00	100·00	100·00

	Vol.	Sp. gr.	Or:	Vol.	Sp. gr.
Nitrogen gas	1	0·9706	Nitric oxide gas	2	2·0798
Oxygen gas	2	2·2186	Oxygen gas	1	1·1093
Hyponitric acid vapour	1	3·1892		1	3·1891

($N^2O^3 + N^2O^5 = 477·04 + 677·04 = 1152·08$. Berzelius.)

This acid is regarded by Berzelius as a compound of nitric and nitrous acid.

Decompositions. Hyponitric acid vapour is not decomposed at a moderate red heat. (Graham.)—1. The vapour mixed with excess of hydrogen gas and passed over spongy platinum, raises the latter to a bright red heat, and yields water and ammonia. (Kuhlmann.) (See also *Ammonia.*) Ignited charcoal burns in hyponitric acid vapour with a dull red flame. Phosphorus, in order to burn it, requires to be heated more strongly than for oxygen gas, but when once set on fire burns with great splendour. According to Dulong, sulphur when strongly heated burns in the acid vapour; but, according to others, it is extinguished. Iodine may be volatilized in hyponitric acid vapour without undergoing oxidation. (Dulong.) The acid has scarcely any action on phosphuretted hydrogen gas. (Graham.)—2. Potassium takes fire in hyponitric acid vapour at ordinary temperatures, and burns with a red flame: sodium also decomposes it, but without disengagement of light or heat; copper, tin, and mercury, at ordinary temperatures, slowly decompose the vapour; if, however, the vapour is passed over iron or copper contained in a tube at a red heat, nitrogen gas and an oxide of the metal are obtained.—3. From an aqueous solution of hydrosulphuric acid, hyponitric acid rapidly precipitates sulphur, with formation of ammonia; it also rapidly decomposes a solution of ammonia.

4. Hyponitric acid is decomposed by water, and converted, by unequal distribution of its oxygen, into nitric acid, on the one hand, and nitrous acid and nitric oxide on the other,—doubtless because the water has little or no affinity for hyponitric acid, but a powerful affinity for nitric acid. The decomposition into nitric and nitrous acids is as follows:

$$2NO^4 = NO^5 + NO^3.$$

The decomposition into nitric acid and nitric oxide is:

$$3NO^4 = 2NO^5 + NO^2.$$

The lower the temperature, and the smaller the quantity of water present, the larger is the proportion of nitrous acid and the smaller that of the nitric oxide. But the nitrous acid, which is produced in preference under these circumstances, may be afterwards resolved by heat, or by the addition of bodies which promote the formation of gas bubbles (I., 275, 3), into nitric acid and nitric oxide:

$$3NO^3 = NO^5 + 2NO^2.$$

With a smaller quantity of water, a portion of the hyponitric acid remains undecomposed, because it combines with the nitric acid already produced, and appears to be thereby protected from the further decomposing action of the small quantity of water present.

When a small quantity of water is added to a large excess of hyponitric acid, the acid acquires a deep green colour, without disengagement of gas. (Dulong.) According to Dulong, the green colour is caused by nitric oxide gas formed at the same time with the nitric acid and remaining partially dissolved; more probably however by the nitrous acid produced, as this compound is blue, and would form a green mixture with the undecomposed hyponitric acid.

When hyponitric acid is added in separate portions to a given quantity of water, the first portions evolve the largest quantity, and the last not even a trace of nitric oxide gas: the water becomes first blue, then green, and lastly orange-yellow. (Gay-Lussac.)—If to 92 parts (2 atoms) of hyponitric acid cooled down to $-20°$, 9 parts (1 atom) of water are slowly added in a fine stream, a small quantity only of nitric oxide gas is evolved, and two strata of liquid are formed, the upper of which is dark green, and the lower, amounting to a third of the whole, of a grass-green colour. The upper stratum begins to boil at $+20°$; but its boiling point quickly rises to 120°, a blue liquid at the same time distilling over in small quantity into the receiver, which must be surrounded with a freezing mixture. [This liquid is probably a mixture of a large excess of hydrated nitric acid with hyponitric and nitrous acids.] The boiling point of the lower stratum ascends gradually from $+17°$ to 28°, at which latter point it remains constant, and a greenish blue liquid distils over (nitric acid with a small quantity of hyponitric), leaving yellow hyponitrous acid in the retort.—If in the same manner, 45 parts (5 atoms) of water are added to 92 parts (2 atoms) of hyponitric acid, in which case the decomposition may take place as follows:

$$2NO^4 + 5Aq = NO^5, 5Aq + NO^3,$$

very little nitric oxide gas is disengaged and two similar strata of liquid are obtained. The upper stratum behaves as in the first experiment; the lower however, from its exceedingly deep bluish green colour, appears transparent only when in thin layers, and enters into violent ebullition even on being poured out from the vessel. When both liquids are distilled together, the lower stratum begins to boil even below 0°; and by the time

that the boiling point has risen to 25°, it is wholly carried over into the receiver (which is surrounded with a freezing mixture) in the form of a blue distillate of nitrous acid. (Fritzsche.)

When hyponitric acid is mixed with 5 times its volume o water at ordinary temperatures, a large quantity of nitric oxide gas is evolved. When this action ceases, the immersion of a platinum wire gives rise to further disengagement of gas; and if heat be applied, the action becomes so violent that the liquid is scattered about. A still more violent and prolonged evolution of gas than that caused by platinum, is produced by metals which are attacked by the acid, such as iron, copper, brass, and silver. The action on the metals is very slight; but the small bubbles of nitric oxide gas which are formed by their oxidation, cause the nitrous acid present likewise to give off nitric oxide gas. Wood-shavings also cause effervescence on account of the air which adheres to them; but if previously boiled in water, they scarcely produce any effect. On mixing one measure of hyponitric acid with 10 measures of water, nitric oxide gas is likewise disengaged. The colourless liquid yields, when boiled, an additional 60 measures of nitric oxide gas; but the evolution of gas continues for the space of an hour: if platinum wire be present, it ceases much sooner. In this mixture, also, the above mentioned oxidable metals produce violent effervescence, whereas they are but feebly attacked by a mixture of one measure of nitric acid and 10 measures of water. If one measure of hyponitric acid is added by drops to 25 measures of boiling water, the whole of the nitric oxide is not immediately evolved; for it is only after long boiling that the liquid ceases to give a brown colour with solution of green vitriol. A mixture of hyponitric acid with an excess of concentrated nitric acid does not evolve gas when mixed with water. (Schönbein.)

5. The alkalís act in a similar manner to water, inasmuch as they also possess little or no affinity for hyponitric, but a very powerful affinity for nitric acid. A concentrated solution of potash yields with hyponitric acid, nitrite and nitrate of potassa, with slight evolution of nitric oxide gas. (Gay-Lussac, Dulong.) Hyponitric acid vapour transmitted at ordinary temperatures over pure baryta, is slowly absorbed; at 200°, the baryta suddenly becomes red-hot, fuses, and is converted, without disengagement of gas, into nitrate and nitrite of baryta. (Dulong.)

Combinations. *a.* With Aqueous Nitric acid.

b. With Salifiable Bases. The only compound known is that with oxide of lead.

E. Nitric Acid. NO^5.

Salpetersaüre, Perfect Nitric Acid, Acide nitrique, Acide azotique, Acidum nitricum.

Sources. In combination with potassa, soda, lime, and magnesia on the surface of the earth where organic matter has undergone decomposition; in numerous springs, in many plants which absorb the nitrates from the soil where they are produced (see Vaudin, *J. Chim. Med.* 8, 674; 9, 321); in rain-water after a thunder-storm. (Liebig.)

Formation.—1. From Nitrogen and Oxygen:—*a.* When a mixture of 3 volumes of nitrogen gas and 7 volumes of oxygen (or more accurately, 2 nitrogen and 5 oxygen) is placed over water or an aqueous solution of potash, and electric sparks passed through it for a week, condensation takes place, and nitric acid is formed. (Cavendish.)—*b.* Platinum wire heated by the electric current in a mixture of nitrogen gas, oxygen gas, and aqueous vapour, till it fuses, gives rise to the production of nitric acid. (H. Davy.)—*c.* When a mixture of 1 volume of nitrogen with 14 of hydrogen is burned in oxygen gas, nitric acid is formed. (Berzelius.)—*d.* Aqueous vapour (mixed with air?) passed over ignited peroxide of manganese, yields nitric acid. (H. Davy.)—*e.* When water containing atmospheric air is decomposed by a current of electricity, traces of nitric acid are formed at the positive pole. (H. Davy.)—A mixture of nitrogen and oxygen gases passed through a red-hot tube, does not yield nitric acid; not even when the tube contains spongy platinum or platinum black; neither is nitric acid formed by passing nitrogen gas either dry or moist, over ignited peroxide of manganese. (Kuhlmann.) A mixture of 2 volumes of nitrogen gas and 5 of oxygen likewise remains unaltered when enclosed in a tube by means of solution of potash and mercury, and immersed in the sea to the depth of 540 metres (or 295 fathoms) though it must then sustain a pressure of 50 atmospheres. (Laroche, *Schw.* 1, 123 & 172.)

2. From Nitrous Oxide, by its decomposition in contact with water, (p. 375, 1.)

3. From Nitric Oxide. *a.* By its decomposition in contact with water. (p. 378, 1.)—*b.* Even with excess of oxygen, nitric oxide forms nitric and not hyponitric acid, only when water or a salifiable base is present. If nitric oxide is passed into oxygen gas confined in a vessel by water at a temperature of 52°, the formation of nitric acid ensues, attended with a slight explosion. (Lampadius, *J. pr. Chem.* 4, 391.)—*c.* With aqueous solution of hypochlorous acid, nitric oxide gas yields nitric acid and chlorine; it acts in a similar manner with the hypochlorites. (Balard.)

4. From Nitrous Acid, by its decomposition in contact with water (see page 381).

5. From Hyponitric Acid.—*a.* In the decomposition of that substance (4 and 5, pp. 385, 386).—*b.* Hyponitric acid is converted into nitric acid, when mixed with water and oxygen gas or with aqueous iodic acid, iodine being set free in the latter case (Gaultier de Claubry); or with hydrated hypochlorous acid, the decomposition being attended with separation of free chlorine. (Balard.)

6. From Ammonia.—*a.* When a mixture of ammoniacal gas with excess of oxygen is transmitted through a red-hot tube, explosion takes place and nitric acid is produced. (Fourcroy.) A mixture of ammoniacal gas and atmospheric air passed through a red-hot glass tube, yields a small quantity of nitric oxide and hyponitric acid; spongy platinum introduced into the tube produces no effect at ordinary temperatures; but if heated to 308° in a current of the mixture, it becomes red-hot, and gives rise to the formation of nitric and hyponitric acids, or if very strongly heated, of the latter only; when the ammonia is in excess, nitrate of ammonia is produced. A mixture of the vapour of carbonate of ammonia with atmospheric air yields less nitric acid than that of pure ammonia with air; sal-ammoniac vapour with atmospheric air yields chlorine, hyponitric acid, and water. (Kuhlmann.)—*b.* Ammoniacal gas

passed over peroxide of manganese ignited in a gun-barrel, yields nitric oxide gas (Milner, *Crell. Ann.* 1795, 1, 554); but if the peroxide of manganese is ignited in a porcelain tube, nitrate of ammonia is obtained. (Morveau, *Schw. J.* 9, 370; Vauquelin, *J. Polytechn. Cah.* 2, 174.) Ammoniacal gas passed over ignited sesqui-oxide of iron also yields a large quantity of nitrate of ammonia. (Liebig, *Mag. Pharm.* 33, 40.)—*c.* A mixture of milk of lime with a small quantity of ammonia enclosed for six weeks in summer in a stoppered bottle containing air and frequently shaken, produces nitric acid. (Collard de Martigny, *J. Chim. Med.*, 3, 525; see also Kuhlmann, *N. Ann. Chem. Phys.* 20, 223.)

7. From organic substances containing nitrogen.—*a.* Cyanogen gas mixed with atmospheric air and passed through a red-hot glass tube containing spongy platinum, yields hyponitric acid and carbonic acid. (Kuhlmann.—*b.* Azotized organic matters exposed to the air in contact with salifiable bases and water, yield salts of nitric acid. The base may even be ammonia, produced in the decomposition of the organic compound. The predisposing affinity of the base for nitric acid causes the nitrogen—at the moment when it is set free by the decomposition of the organic matter, and before it has assumed the gaseous form, that is to say, while it is in the *nascent state* (I, 37, 38)—to unite with the oxygen of the air, and form nitric acid.—Kuhlmann supposes that, in the formation of nitric acid, when the mixture contains no carbonate of potassa, but only carbonate of lime and carbonate of magnesia, ammonia is first formed from the nitrogen disengaged by the decomposing organic matter; that the ammonia produces nitrate of ammonia by taking up oxygen from the air; and that the latter salt then undergoes double decomposition with the carbonates of lime and magnesia, giving rise to nitrate of lime and magnesia and carbonate of ammonia. According to this theory, the ammonia is at the same time the source of the nitric acid, and the vehicle of its transference to the fixed salifiable bases. In crude saltpetre-ley, Kuhlmann always detected ammonia, partly combined with carbonic acid and partly with fixed acids. The observation of Collard de Martigny above referred to also corresponds with this view.—Dried plants and their extracts, exposed for months or years to the influence of moist air, become much richer in nitrates than in the fresh state, in consequence of the gradual decomposition of the nitrogenous compounds which they contain; and the solution obtained by exhausting them with water, frequently evolves nitric oxide gas when boiled, (Braconnot, *Ann. Chim. Phys.* 35, 261; also *Pogg.* 10, 506; Planche *J. Pharm.* 23, 548; Vaudin, *J. Chim. Med.* 8, 674; 9, 321.) According to Saussure (*Bibl. Univ.* 56, 130), the nitrogen of the air is likewise concerned, in this case, in the formation of nitric acid. Longchamp (*Ann. Chim. Phys.* 33, 5; 34, 215) is of opinion that organic azotized compounds have nothing to do with the formation of nitre, but that the water contained in porous bodies, such as chalk, absorbs oxygen and nitrogen from the air and condenses them in the form of nitric acid. The observation of Gaultier de Claubry (*Ann. Chim. Phys.* 52, 24), that a very large quantity of nitrates is produced in chalk hills, which contain but a trace of organic matter, is in favour of this view. It may, however, be admitted that, under certain circumstances, namely, during electric disturbances in the air (vid. *Atmospheric air*), the nitrogen, the nitric acid, and the carbonate of ammonia contained in the atmosphere may assist in the formation of nitre—without at the same time denying, that the nitrogen contained in organic matter plays

by far the most important part in the ordinary production of nitre. (Gay-Lussac, *Ann. Chim. Phys.* 34, 56; see also Fontenelle, *J. Pharm.* 10, 14.)

¶ *Preparation.* By treating perfectly dry nitrate of silver with perfectly dry chlorine, and condensing the liberated acid vapour by a freezing mixture. The nitrate of silver is placed in a U-tube capable of containing about 500 grammes (15 or 16 oz.) of the salt. This tube is connected with another U-tube of considerable size, and having at the bottom a small spherical reservoir, which serves to receive a very volatile liquid (nitrous acid?), produced in the course of the operation. The tube containing the nitrate of silver is immersed in water covered with a thin layer of oil and heated by means of a spirit lamp, which communicates with a reservoir kept at a constant level. The chlorine is evolved from a glass gasometer, and its displacement is regulated by a slow and constant flow of sulphuric acid; it is dried by passing over chloride of calcium and then over pumice-stone moistened with sulphuric acid. The bend of the large U-tube is immersed in a freezing mixture. The nitrate of silver is first heated to 180° (356° F.) and deprived of moisture by passing a current of dry carbonic acid gas through the apparatus. After this, the transmission of the chlorine is commenced. At ordinary temperatures it appears to exert no action; but when the nitrate of silver is heated to 95° (203° F.), and the temperature then lowered to 58°—68° (136°—154° F.), the decomposition of the nitrate takes place, chloride of silver being formed, and nitric acid and oxygen evolved. At first a portion of hyponitric acid is developed, but as soon as the temperature has reached its lowest point, crystals of anhydrous nitric acid are formed and soon obstruct the U-tube. The temperature produced by the use of ice alone is low enough for the production of these crystals. The gases evolved during the process are coloured; and in the spherical reservoir at the bottom of the tube, there collects a small quantity of liquid which must be removed from the apparatus before transferring the nitric acid to another vessel. To effect this transference, the current of chlorine must be replaced by a current of carbonic acid; the condensing tube must no longer be cooled; and the bulb destined to receive the crystals must be immersed in a freezing mixture and connected with the U-tube by means of a caoutchouc tube lined with asbestos. The chlorine should pass very slowly, not more than 3 or 4 litres (about 60 cub. in.) in 24 hours. An apparatus arranged as above described will go on day and night without superintendence: it is merely necessary to renew the supply of sulphuric acid which displaces the chlorine, the alcohol which feeds the lamp, and the freezing mixture. (Deville; vid. *Chem. Gaz.* Apr. 2, 1849.)

Properties. Anhydrous nitric acid forms transparent colourless crystals of great brilliancy, having the form of prisms with six faces and apparently derived from a right rhombic prism. When slowly deposited in a current of the gas strongly cooled, they attain a considerable size. They melt a little above 30° (85° F.), and boil at about 45° (113° F.). At 10° (50° F.) the tension of the vapour is very considerable. At temperatures near the boiling point, decomposition appears to begin: hence the tension of the vapour cannot be determined by Dumas' process. (Deville.) ¶

		Calculation.		Lavoisier.	Cavendish.	Berzelius.	Davy.
N	....	14	.... 25·9	 20	 25	 26	.... 29·5
5O	....	40	.... 74·1	 80	 75	 74	.... 70·5
NO^5	....	54	........100·0	 100	 100	 100	.... 100·0

	Vol.	Or,	Vol.
Nitrogen gas	2	.... Nitric oxide gas	4
Oxygen gas	5	.... Oxygen gas	3

(N^2O^5 = 2 . 88·52 + 500 = 677·04. Berzelius.)

Combinations. a. Aqueous Nitric acid. In the concentrated state: *Spirit of Nitre, Salpetergeist, Spiritus nitri acidus;* in the dilute state: *Aqua fortis, doppeltes und einfaches Scheidewasser.*

¶ *Formation.* By dissolving anhydrous nitric acid in water. The crystals dissolve completely, causing great rise of temperature, but no disengagement of gas or production of colour. The solution saturated with baryta and evaporated, yields crystals of nitrate of baryta. ¶.

Preparation.—1. From Nitrate of Potash. 100 parts of purified saltpetre are distilled in a glass retort with 96 parts of common oil of vitriol, till the residue in the retort becomes tranquil, and no more drops distil over. The receiver, which is cooled with water and not attached to the retort by any cement, is changed as soon as the acid which passes over ceases to give a cloud with nitrate of silver. The first receiver contains nitric acid contaminated with chlorine; the second, nitric acid in a state of purity.

The ingredients should be but little more than sufficient to half fill the retort, or there will be danger of the mixture boiling over. When a tubulated retort is employed, the oil of vitriol is introduced through the tubulus; but with a plain retort, the acid is poured down the neck by means of a bent tube-funnel, care being taken not to soil the neck with the oil of vitriol. The neck of the retort must reach almost to the middle of the receiver, and must be attached to it without any cement. The receiver must be surrounded with cold water, or, together with the neck of the retort, enveloped in bibulous paper kept constantly wet by a stream of water from a dropping bottle. (*App.* 36.)

Nitre, even when purified, contains chloride of potassium or sodium, which at the commencement of the process gives rise to the evolution of a yellowish-red mixture of hyponitric acid vapour and chlorine gas.

$$KO, NO^5 + NaCl + 2SO^3 = KO, SO^3 + NaO, SO^3 + NO^4 + Cl.$$

As the whole of the chlorine passes over at the beginning of the distillation, an acid is at length obtained perfectly free from chlorine; this pure acid amounts to one-half or two-thirds of the whole. It is well to change the receiver as soon as the acid drops which fall from the neck of the retort, produce but a slight turbidity in a solution of nitrate of silver, and again, when they cease to cause any turbidity whatever. If the nitre be purified by repeated crystallization (according to the method described in page 15, vol. I.) from every trace of chloride, it yields a perfectly pure acid from the commencement.

For every atom of nitre (= 101·2 parts) 2 atoms of oil of vitriol (= 98 parts) are required; in which case, 1 atom of water passes over with 1 atom of nitric acid, and bisulphate of potassa with 1 atom of water remains in the retort.

$$KO, NO^5 + 2(HO, SO^3) = KO, HO, 2SO^3 + HO, NO^5.$$

As 101·2 parts (1 atom) of nitre contain 54 parts (1 atom) of nitric acid, and the latter combines with 9 parts (1 atom) of water, 100 parts of nitre should yield 62·25 parts of acid. But in reality a larger quantity is obtained; because, according to Hess (*Pogg.* 53, 537), the monohydrated acid (HO, NO^5) distils over at the commencement only, and afterwards the bihydrated acid ($2HO, NO^5$), the bisulphate of potassa, when strongly heated, giving up part of its water to the nitric acid. Accordingly, Bucholz (*Taschenb*, 1819, 201) who, following Süersen's directions, distilled 100 parts of nitre with 95 parts of oil of vitriol, obtained 65·6 parts of nitric acid. Geiger (*N. Tr.* 3, 1, 456), obtained from 100 parts of nitre and 95·83 parts of oil of vitriol, 68·75 parts of nitric acid and 126·04 parts of residue. R. Phillips (*Ann. Phil.* 30, 429; also *Kastn. Arch.* 13, 198), obtained from 100 parts of nitre and 100 parts of sulphuric acid of 1·844 specific gravity, 65·9 parts of an acid of 1·5035 specific gravity, which for every 54 parts (1 atom) of anhydrous acid, contained 13·5 parts (1½ atoms) of water—and a residue of bisulphate of potash, amounting to 198·6 parts. (Loss = 1·4 parts.)—Mitscherlich (*Pogg.* 18, 152) also found the proportion of 98·6 parts of oil of vitriol to 100 parts of nitre, the most suitable. The mixture becomes pasty when heated, and at a temperature of 120° to 125°, (248°—257° F.), readily gives off nitric acid of specific gravity 1·522, at 12·5° (54·5° F.).—More than 2 atoms of oil of vitriol to 1 atom of nitre, does not facilitate the disengagement of the nitric acid, and towards the end of the distillation, may cause the latter to be contaminated with sulphuric acid. If 1 atom of nitre be distilled—as was formerly the practice—with only 1 atom of oil of vitriol (100 parts to 48 parts), the first half of the nitric acid is disengaged with facility, since the sulphuric acid decomposes half of the nitre as above,

$$2(KO, NO^5) + 2HO, SO^3 = KO, NO^5 + KO, HO, 2SO^3 + HO, NO^5;$$

but the bisulphate of potassa thus produced, decomposes the rest of the nitre, at a temperature, which, according to Mitscherlich, is not below 220° (428° F.); and at that degree of heat, a great portion of the acid evolved, is resolved into hyponitric acid vapour and oxygen gas, so that the acid first distilled over is converted, by absorption of hyponitric acid, into red fuming nitric acid.

Diluting the oil of vitriol with water has no other effect than to render necessary the employment of more fuel and condensing water, and increase the difficulty of getting rid of the chlorine. Mitscherlich recommends for 100 parts of nitre, a mixture of 96·8 parts of oil of vitriol and 40·45 parts of water; the mixture becomes liquid, distils tranquilly at a temperature of 130° to 132°, and yields throughout the process an acid of specific gravity 1·40. By using fuming oil of vitriol, a portion of the nitric acid is resolved, from deficiency of water, into hyponitric acid and oxygen gas. Any arsenious acid which may be contained in the oil of vitriol, remains behind in the residue, without contaminating the nitric acid.

2. From commercial Nitrate of Soda—Chili saltpetre. 100 parts (1 atom) of nitrate of soda are distilled in the same manner as above, with 58 parts (1 atom) of oil of vitriol.—With soda-nitre, 2 atoms of sulphuric acid are not required; the decomposition takes place at a lower temperature, and the acid obtained is of a pale yellow colour. (Graham, *Lehrb.* 2, 69.) If two atoms of oil of vitriol are employed, the acid must be diluted with one-fourth its weight of water, to prevent the mass from boiling over; the best proportions are, 100 parts of nitrate of soda, 116·7

parts of oil of vitriol and 30 parts of water; for the bisulphate of soda retains not only 1 atom of water, like the potash-salt, but 3 atoms, which it tends to separate from the nitric acid, so that the mass becomes solid, and the acid is partly resolved into hyponitric acid and oxygen gas. (Wittstein, *Repert*, 64, 289.)

On the large scale, the potash or soda nitre is distilled in horizontal cast iron cylinders, or similar vessels. Formerly, calcined green vitriol or moistened clay was substituted for sulphuric acid in this process; the greater part of the acid then distilled over as hyponitric acid, which, when condensed by the water, yielded *aqua fortis* (*Scheidewasser.*)—The ordinary acid may be purified by distillation with a small quantity of nitre—the receiver being changed in the course of the process. Acid containing chlorine passes over first, and afterwards pure nitric acid.

Or, in order to obtain an acid as concentrated and as free as possible from chlorine and hyponitric acid, Millon distils it till a third part has passed over, and then distils the rest with an equal measure of oil of vitriol, the receiver being changed. The latter distillate he purifies by a second distillation from the sulphuric acid which comes over; heats the distillate to the boiling point in the bottle in which he intends to preserve it; and passes a continuous current of carbonic acid gas through it, till the acid becomes cold. Should the specific gravity of the acid exceed 1·5, the heating and current of carbonic acid gas must be repeated once or twice, to remove the whole of the hyponitric acid. In this manner a transparent and colourless acid may be obtained of specific gravity 1·521, and containing 15·02 per cent. (1 atom) of water.

Impurities in Nitric acid.—Hyponitric acid: The concentrated acid is coloured yellow or yellowish red by this substance; but the very dilute colourless acid may also be contaminated with it. When an acid which contains hyponitric acid, is diluted with 2 or 3 parts of water, it precipitates sulphur from an aqueous solution of hydrosulphuric acid or of an alkaline hydrosulphate, and iodine from alkaline iodides; colours ferrous salts brown, and ferrocyanide of potassium green; and decolorizes a solution of indigo, at a degree of dilution at which pure nitric acid ceases to have any effect on it. (Millon.)—The greater part of the hyponitric acid may be expelled by boiling for a short time in a retort, when nitric acid mixed with hyponitric acid passes over.—Pelouze digests the acid with peroxide of lead; if concentrated, it does not dissolve any of the lead.—Millon distils it mixed with $\frac{1}{100}$ of its weight of bichromate of potash; if, however, the acid has a greater specific gravity than 1·48, it will again be partially resolved by distillation into oxygen gas and hyponitric acid; when this happens, Millon treats it with carbonic acid gas aided by heat, as already described.

Chlorine. The acid precipitates a solution of silver. The concentrated acid may likewise be freed from this impurity by heat, the chlorine, together with the hyponitric acid and a portion of nitric acid, distilling over first.—The old method of preparing the *precipitated* or *chemically pure nitric acid* is rather troublesome: the dilute acid is precipitated by nitrate of silver, decanted from the insoluble chloride of silver, and purified from the excess of nitrate of silver by distillation. Bescherer (*J. pr. Chem.* 16, 317), recommends that the acid containing chlorine be distilled over metallic silver; in this case, however, some of the chlorine may still pass over with the nitric acid. The acid cannot be purified from chlorine by means of oxide of lead, because the

chloride of lead dissolves in the nitric acid, and is again decomposed on the application of heat.

Sulphuric Acid: From soiling the neck of the retort, spirting of the mixture, or from using too large a quantity of oil of vitriol, and heating too strongly. The nitric acid diluted with water precipitates chloride of barium.—*Purification*—by redistilling from a small quantity of nitre, or precipitating the previously diluted acid with pure nitrate of baryta and distilling the decanted liquid. If chlorine and sulphuric acid are both present, the purification must be effected by precipitating with nitrate of silver and nitrate of baryta, decanting, and distilling.

Iodine: In the acid prepared from Chili saltpetre, as the latter substance contains iodine (page 247); hence this impurity is present in much of the ordinary nitric acid of commerce. An acid of this kind, when distilled with oil of vitriol, yields a sublimate of iodine after all the nitric acid has passed over. If it be neutralized with potassa, mixed with solution of starch, and oil of vitriol slowly added drop by drop, the liquid assumes a blue colour; chlorine does not produce this effect. (Lembert, *J. pr. Chem.* 28, 297.)

Potash and Soda salts, Sesquioxide of iron, and other *fixed substances,* are left behind on evaporating the acid.

Concentration of Nitric acid.—1. An acid whose specific gravity is below 1·40 yields when distilled, a weaker acid, till the residue in the retort has acquired a specific gravity of 1·42 (Dalton), 1·415 (Tünnermann, *Kastn. Arch.* 19, 344), 1, 405, (Millon), 1·40 (Mitscherlich).—2. An acid of specific gravity 1·55 yields, at the beginning of the distillation, an acid of 1·62, and then an acid of 1·53; the residual acid having a specific gravity of 1·49. (Proust.) The acid of specific gravity 1·522, as obtained by the distillation of 100 parts of nitre with 96·8 parts of oil of vitriol, yields, when partially distilled alone, a distillate of 1·54 and a residue of 1·521. (Mitscherlich.)—3. An acid of specific gravity 1·3032 distilled with a fourth of its volume of oil of vitriol, yields an acid of 1·499; and this again distilled with the same quantity of oil of vitriol, yields an acid of 1·510 at 18°. (Gay-Lussac.) Acid of 1·41 distilled with two parts of oil of vitriol at a gentle heat yields acid of 1·5254, consequently the bihydrated acid. (Tünnermann.) During the distillation with oil of vitriol, the temperature should not rise above 140° or 150°; otherwise decomposition of the acid will ensue: by repeated distillation with oil of vitriol, an acid is obtained of specific gravity 1·520, and boiling at 86° to 88°. (Pelouze, *Ann. Chim. Phys.* 77, 51.) The acid concentrated by means of oil of vitriol is purified from any sulphuric acid mixed with it, by distilling it alone or with nitre.

Properties. Colourless, transparent liquid (frequently however coloured yellow by hyponitric acid). Its highest specific gravity is 1·62 [?] (Proust), 1·564 (Kirwan, Mitscherlich), 1·552 at 20°, (Millon), 1·55 (H. Davy), 1·52 (Pelouze), 1·513 (Thénard); the less water it contains the higher is its specific gravity. Acid of specific gravity 1·30 freezes at —19° (Dalton); a stronger acid requires a temperature of—54°, when it solidifies to a mass like butter. The strongest acid boils below 100°, and is rendered weaker by boiling, in consequence of strong acid being evolved; a more dilute acid boils at a temperature higher than the boiling point of water, and becomes stronger by boiling, a weaker acid being

evolved. According to Dalton, an acid of specific gravity 1·42, becomes neither stronger nor weaker by boiling; and its boiling point is at the highest not above 120° (248° F.). According to Mitscherlich, an acid of specific gravity 1·40 behaves in the following manner; it contains 56 per cent. of acid, and boils between $120\frac{3}{4}$° and 121°; but if platinum wire is not put into it the ebullition becomes percussive, and the temperature may even rise as high as 125°. This percentage of acid approaches nearest to the proportion of 1 atom of nitric acid to 5 atoms of water; the mutual condensation appears then to be greatest in a mixture, in which the acid and water contain the same amount of oxygen. Graham (*Ann. Pharm.* 29, 12) and Bineau (*Ann. Chim. Phys.* 68, 417) suppose that the acid which remains after distillation contains not 5 but 4 atoms of water. According to Millon, a stronger acid is reduced by prolonged boiling in a retort, to a density of 1·419 at the lowest; such an acid contains 4 atoms of water; a weaker acid never attains a density higher than 1·405, corresponding to $4\frac{1}{2}$ atoms of water. When a dilute acid is boiled without platinum wire, the boiling point quickly rises as high as 125° or 128°, at which temperature acid of 1·2 distils over; if platinum wire be then introduced into the retort, the boiling point sinks to 122·5° and the acid which passes over has a specific gravity of only 1·175: it is therefore decidedly weaker than the earlier distillate. Acid of specific gravity 1·522 boils at 86°. (Mitscherlich.) The boiling point, however, gradually rises to 123°, at which temperature, a small quantity of acid of specific gravity 1·484, containing 2 atoms of water, is obtained. (Millon.)

Aqueous nitric acid has a faint, but characteristic odour, and a very sour taste; it colours litmus red; exerts a highly caustic and corrosive action or organic substances, and stains those containing nitrogen, such as the skin and nails, of a yellow colour. The concentrated acid absorbs water from the atmosphere, but less greedily than sulphuric acid. Acid of specific gravity 1·526, evolves heat when mixed with snow; acid of specific gravity 1·420, on the contrary, produces cold with snow, but still evolves heat when mixed with water.

Aqueous nitric acid when heated dissolves copper filings, with evolution of nitric oxide gas which produces yellowish red vapours in the air. The resulting solution is green; and when moderately concentrated, attacks tinfoil, with rise of temperature and effervescence, producing a white powder which evolves ammonia when treated with potash.—Mixed with hydrochloric acid, it dissolves gold leaf (the limit of this reaction is attained when 1 part of nitric acid of specific gravity 1·32 is diluted with 239 parts of water, the solution then requiring 24 hours for its completion; Harting, *J. pr. Chem.* 22, 48);—with oil of vitriol to which a solution of ferrous sulphate has been added, it forms a red mixture;—it changes the blue colour of solution of sulphate of indigo to brownish-yellow, especially when aided by heat.

Calculation of the first, second, third, fourth, and fifth hydrates of nitric acid.

NO^5	1	54	85·71	1	54	75	1	54	66·67	1	54	60	1	54	54·55
HO	1	9	14·29	2	18	25	3	27	33·33	4	36	40	5	45	45·45
	1	63	100·00	1	72	100	1	81	100·00	1	90	100	1	99	100·00

Amount of Pure or Anhydrous Nitric acid in Aqueous Nitric Acid of various strengths.

According to Kirwan and Dalton.			According to Ure (*Schw.* 35, 446).			
Sp. gr.	Per cent. of Acid.	Boiling Point.	Sp. gr.	Per cent. of Acid.	Sp. gr.	Per cent. of Acid.
1·62	82·7	38°?	1·5000	79·700	1·2887	39·053
1·54	72·5	80?	1·4940	77·303	1·2705	36·662
1·50	68·0	99	1·4850	74·918	1·2523	34·271
1·45	58·0	115	1·4760	72·527	1·2341	31·880
1·42	54·4	120	1·4670	70·136	1·2148	29·489
1·40	51·2	119	1·4570	67·745	1·1958	27·098
1·35	44·3	117	1·4460	65·354	1·1770	24·707
1·30	37·4	113	1·4346	62·936	1·1587	22·316
1·26	32·3	111	1·4228	60·572	1·1403	19·925
1·22	28·5	109	1·4107	58·181	1·1227	17·534
1·20	25·4	108	1·3978	55·790	1·1051	15·153
1·18	23·0	106	1·3833	53·399	1·0878	12·752
1·17	21·0	105	1·3681	51·063	1·0708	10·361
1·16	19·3	104·5	1·3529	48·617	1·0540	7·970
1·15	17·8	104	1·3376	46·226	1·0375	5·579
1·14	16·6	104	1·3216	43·833	1·0212	3·188
			1·3056	41·444	1·0053	0·797

According to Mitscherlich, acid of specific gravity 1·54 contains 88·82; acid of specific gravity 1·522, 86·17; and acid of specific gravity 1·40, 44 per cent. of anhydrous nitric acid.—(Richter's Tables, *Stöchiometric*, 3, 64.)

Decompositions.—1. *a.* Nitric acid transmitted through a porcelain tube heated to whiteness, is resolved into oxygen gas, nitrogen gas, and an acid of less strength.—*b.* If the porcelain tube is but feebly ignited, the nitric acid is resolved into oxygen and hyponitric acid. Acid of specific gravity 1·522 (Mitscherlich), and monohydrated nitric acid (HO, NO^5) is partially decomposed even by distillation, with formation of yellowish red vapours. The sun's rays also decompose an acid of specific gravity not less than 1·4; the liquid assumes a yellow colour and evolves oxygen gas. (Scheele; Gay-Lussac.) According to Millon, the monohydrated acid becomes coloured in the sun's rays, only when its temperature reaches 30° or 40°.—*c.* A weaker acid mixed with oil of vitriol, likewise undergoes decomposition on exposure to the sun's rays. (Gay-Lussac.) When a mixture of nitric acid with 4 parts of oil of vitriol is gently heated, the nitric acid is given off in the form of oxygen gas and hyponitric acid, leaving dilute sulphuric acid behind. (Thénard.)—100 parts of nitric acid of specific gravity 1·448 distilled with 500 parts of oil of vitriol at a gentle heat yield 88 parts of nitric acid of specific gravity 1·520; the latter freed by moderate heat from the hyponitric acid which it contains, mixes with 6½ times its volume of oil of vitriol, without perceptible rise of temperature; and the colourless mixture, which emits white fumes, yields, when distilled below 150°, (302° F.) nitric acid of specific gravity 1·520. The same results ensue after a third distillation with oil of vitriol: so that the oil of vitriol does not separate the last portions of water from the nitric acid, nor does it in any way effect its decomposition;—but the heat employed in distillation

decomposes a small quantity of the acid. (Pelouze, *Ann. Chim. Phys.* 77, 51.)

2. *a.* Hydrogen gas does not affect nitric acid at ordinary temperatures; but when transmitted together with its vapour through a red-hot porcelain tube, it gives rise to violent detonation and separation of nitrogen gas. (Fourcroy.) Hydrogen gas charged with vapour of nitric acid and passed over spongy platinum raises it to a red heat, and yields water and ammonia. (Kuhlmann.)—*b.* Diamond is not oxidized by boiling nitric acid. Ignited charcoal burns vividly in contact with the concentrated acid.—*c.* Nitric acid gently heated with boron, yields boracic acid, nitric oxide gas, and nitrogen gas. (Gay-Lussac and Thénard.)—*d.* Phosphorus is dissolved by nitric acid of specific gravity 1·2 on the application of a gentle heat, nitric oxide gas and a small quantity of free nitrogen being evolved, the temperature of the liquid rising, and the phosphorus being converted into phosphorous and phosphoric acids (the statement of Wittstock, *Berl. Jahresb.* 33, 2, 142, that nitrous oxide gas is also formed, is not in accordance with the author's own observations); on evaporating the solution, the phosphorous acid is wholly oxidized by the remaining nitric acid, and converted into phosphoric acid, the change being attended with evolution of nitric oxide gas.—Ammonia is not formed in this reaction. (L. A. Buchner.) Concentrated nitric acid effervesces violently with phosphorus at ordinary temperatures,—the action increasing in violence till the heat disengaged is sufficient to ignite the phosphorus, which then burns in the acid vapours with great splendour. Even the strongest nitric acid at first converts a portion of the phosphorus into phosphorous acid. (Schönbein.) Paper moistened with concentrated nitric acid and laid on a flat piece of phosphorus, detonates when struck with a hammer. (Brugnatelli.) Phosphoric oxide dissolves in dilute nitric acid more rapidly than phosphorus itself; according to Pelouze, the concentrated acid inflames it. Phosphorous acid is converted by nitric acid into phosphoric acid, the action being attended with evolution of nitric oxide gas. Phosphuretted hydrogen gas is violently decomposed by concentrated nitric acid. (Graham.)—*e.* Sulphur is oxidized with some difficulty by nitric acid and converted into sulphuric acid; the action however is more rapid in proportion as the sulphur is more finely divided and the acid stronger. Dilute nitric acid repeatedly saturated with sulphurous acid converts the latter into sulphuric acid. (*Vid.* Dana, *Phil. Mag. J.* 3, 120.) If half an ounce of nitric acid be poured into a bottle full of hydrosulphuric acid gas, a blue flame bursts with a slight noise from the mouth of the bottle, after a few seconds; at the same time, red fumes are produced, the hydrogen and part of the sulphur are oxidated, and the rest of the sulphur is separated in the free state. If sulphuretted hydrogen gas is passed for several hours through a mixture of 1 measure of concentrated nitric acid and from 2 to 4 measures of water, heat is generated, nitric oxide gas is disengaged, and sulphur separated; and the liquid is afterwards found to contain sulphate of ammonia and free sulphuric acid. (Johnston, *N. Ed. J. of Sc.* 6, 65; also *Schw.* 64, 301; also *Pogg.* 24, 354.) Nitric acid perfectly free from hyponitric acid does not decompose an aqueous solution of hydrosulphuric acid at ordinary temperatures. (A. Vogel, Millon.)—*f.* Selenium is converted by warm nitric acid into selenious acid. (Berzelius.)—*g.* Iodine, gently heated with highly concentrated nitric acid, yields iodic acid and fumes of hyponitric acid. Hydriodic acid and nitric acid act upon each other in such a manner as to produce water, iodine, and nitric oxide:

$$3HI + NO^5 = 3HO + 3I + NO^2.$$

—*h*. Aqueous hydrochloric acid and nitric acid form chlorine, water, and hyponitric acid. (Vid. *Aqua regia.*)—*i*. Nitric acid absorbs nitric oxide gas in greater abundance, the smaller the quantity of water it contains and the lower the temperature; and is converted, by giving up oxygen to the nitric oxide, into hyponitric acid and nitrous acid, the colour of the mixture becoming first yellow, then green, and lastly blue.

$$2NO^5 + NO^2 = 3NO^4 \text{ and } NO^5 + 2NO^2 = 3NO^3.$$

—Nitric acid of specific gravity 1·115 absorbs but little of the gas at ordinary temperatures, and remains colourless; acid of specific gravity 1·32 becomes green; acid of 1·41, orange; and acid of specific gravity 1·5 acquires a dark-reddish colour; the latter mixture when heated generally evolves hyponitric acid. (Thénard.) When a current of nitric oxide gas is passed through nitric acid containing more than 5 atoms of water and surrounded with a freezing mixture, a blue liquid is formed, from which blue nitrous acid may be obtained by distillation; when less than 5 atoms of water is present, a yellow liquid is produced containing hyponitric acid. (Fritzsche.) According to Priestley (*Experim. and Observat.* 3, 121), strong nitric acid, by absorbing nitric oxide, becomes first yellow, then orange, then olive-green, then light-green, and lastly greenish blue; the bulk and volatility of the acid are at the same time considerably increased, and a dense red vapour is evolved*.—*k*. [For the decomposition with ammonia, see *Nitrate of Ammonia.*]

3. Nitric acid, at ordinary temperatures or at the boiling point, oxidizes all metals, excepting silicium, titanium, tantalum, platinum, rhodium, and iridium, and (under ordinary circumstances,) gold. The resulting metallic oxides (except those of tungsten, tellurium, tin, and arsenic) combine with the undecomposed portion of the acid and form salts which (with the exception of nitrate of antimony) dissolve in the liquid, provided at least it is not too concentrated. In this reaction, the portion of acid which oxidizes the metal is converted sometimes into hyponitric acid, sometimes into nitric oxide (*Sch.* 24), nitrous oxide (*Sch.* 25), or nitrogen gas, or—if the metal at the same time decomposes water, the hydrogen of which then combines with the nitrogen of the acid—into ammonia. (*Sch.* 85.) The last-mentioned re-action takes place with tin, and likewise, according to Kuhlmann (*Ann. Pharm.* 27, 27), with zinc, cadmium, and iron. Which of the above products is formed, depends partly on the affinity of the metal for oxygen, partly on the temperature and concentration of the acid.

At ordinary temperatures, nitric acid converts tin into binoxide, with great rise of temperature and evolution of nitric oxide, nitrous oxide, nitrogen, and ammonia. When 1 part of tin is digested with 16 parts of nitric acid of specific gravity 1·2, the large excess of acid prevents the temperature from a rising beyond 33°, and consequently, perfectly pure nitrous oxide gas is disengaged, though not in great abundance; with a smaller proportion of acid, in which case the heat rises to 44°, the nitrous oxide is mixed with nitric oxide gas. Nitric acid of specific gravity 1·2 diluted with from one to three times its bulk of water, evolves pure nitrous oxide gas when acted upon by zinc; when not diluted, it yields nitrous oxide gas contaminated with nitric oxide, the quantity of the latter increasing

* The conversion of nitric acid into hyponitric acid by the action of nitric oxide gas, and the decomposition of hyponitric acid by water into nitric acid and nitric oxide gas, induced Priestley, Berthollet, Sir H. Davy, and Thomson, to regard hyponitric acid, not as a direct compound of nitrogen with oxygen, but as a combination of nitric acid with nitric oxide.

as the temperature rises. Nitric acid of specific gravity 1·2 diluted with three times its bulk of water, does not attack iron at ordinary temperatures; if diluted with only twice its bulk, it first evolves nitrous oxide gas mixed with a small quantity of nitric oxide, but towards the end of the action, the latter compound only is disengaged. (Pleischl.) When copper is digested in nitric acid of specific gravity 1·217 at a temperature of $-10°$ (and this temperature is kept up), nitrous oxide is evolved, mixed with a small quantity of nitric oxide gas (Millon); dilute nitric acid acted upon by copper at ordinary temperatures evolves pure nitric oxide gas; but if the temperature rises, or the acid is more concentrated, nitrogen is likewise disengaged. Antimony, bismuth, lead, mercury, and silver liberate nitric oxide gas; but if heat is applied or if the acid is strong, nitrogen gas is likewise evolved.

The transference of the oxygen from the nitric acid to the metal, is always attended with evolution of heat, by which the process of oxidation —slow at first—becomes accelerated, and sometimes ends in actual combustion. Concentrated nitric acid poured on heated iron filings or on melted bismuth, zinc, or tin, causes the metal to become incandescent. (Proust.)

Nitric acid vapour transmitted over ignited metals, yields metallic oxide with nitrogen and hydrogen gases, if the metals are capable of decomposing water,—when this is not the case, the products are metallic oxide, nitrogen gas and water.

Woodhouse first pointed out that certain metals, such as tin, copper, and silver, remain unchanged in highly concentrated nitric acid, but are instantly oxidized on the addition of water. The circumstances under which these anomalies and the so-called passive condition of various metals are produced, have been already discussed (I. 353—363), where it has been shown that the formation of a thin stratum of oxide or nitrate on the surface of the metals, is in all probability the cause which prevents the further action of the acid. The following observations likewise tend to the same conclusion.

Tin is not attacked by very strong nitric acid, even on boiling. Strong boiling nitric acid does not dissolve a trace of lead or silver, inasmuch as the nitrates of lead and silver are insoluble in that menstruum. Zinc, bismuth, copper, and mercury, on the contrary, dissolve in strong nitric acid, though less readily than in the same acid when more dilute, because their salts are more or less soluble in the concentrated acid. But nitric acid mixed with alcohol acts but feebly on bismuth, zinc, and copper, and not at all on mercury, because the nitrates of the first three metals are but slightly soluble, and that of mercury perfectly insoluble in alcohol. (Braconnot, *Ann. Chim. Phys.* 52, 286; also *Pogg.* 29, 173.)

Nitric acid, for the most part, oxidizes metals only when it contains nitrous acid. The latter first gives off nitric oxide and forms a nitrite, which at the moment of its formation is converted by the nitric acid into a nitrate. The nitrous acid thus set free, together with that produced by the action of the nitric oxide on the nitric acid, again acts upon a fresh quantity of metal, forming nitric oxide and a metallic nitrite, &c. In this manner the quantity of the nitrous acid continually increases, and with it also the intensity of the chemical action. [Although nitrous acid contains less oxygen than nitric acid, it appears to part with that element more readily, because its affinity for water is less than that of nitric acid; *vid.* I., 144.] At $-18°$ ($-0°$ F.) monohydrated or bihydrated nitric acid (free from nitrous acid) does not act on *zinc;* but the metal becomes

covered with a yellowish white film, which probably prevents further action: at a few degrees above $-18°$, however, the film appears to be dissolved; for as soon as the vessel is taken out of the freezing mixture, a violent action commences. In an acid containing 4 or $4\frac{1}{2}$ atoms of water, the zinc retains its metallic lustre, and remains unaltered at $-18°$, but at $0°$ it is violently attacked. Still weaker acid acts even at $-18°$. Polished balls of *iron* immersed in nitric acid containing from 1 to 2 atoms of water, and free from nitrous acid, become covered, sometimes with a black, sometimes with a blue or blue and yellow film, which has the properties of ferroso-ferric oxide as produced by the rusting of iron. In this state they are not attacked by a weaker acid, unless the temperature is raised. An acid containing 4 or $4\frac{1}{2}$ atoms of water does not affect the metallic lustre of iron, or attack it in any way, unless aided by heat. A still weaker acid dissolves the iron, though but slowly, forming a green solution [owing to the presence of nitric oxide which is absorbed by the ferrous nitrate]. Nitric acid, of whatever degree of concentration, if free from nitrous acid, does not attack *arsenic* or *antimony* at the temperature of $20°$ ($68°$ F.); only the strongest acid acts slightly on antimony, but without effervescence. *Bismuth* retains its metallic lustre at $+20°$ in bihydrated nitric acid free from nitrous acid; it is rapidly dissolved in acid containing 4 or $4\frac{1}{2}$ atoms of water; but remains unattacked in acid of specific gravity 1·108. In the latter case, heat or a current of nitric oxide gas sets up the action, but it may be arrested again by surrounding the vessel with a freezing mixture, or by the addition of ferrous sulphate. *Tin* behaves in a similar manner to bismuth. Acid of specific gravity 1·07, and not containing nitrous acid, does not attack *copper* at $+20$ (but hot acid of sp. gr. 1·07, or stronger acid acts on the copper); a current of nitric oxide gas or the addition of a few drops of nitrite of potassa sets up the action; the larger the quantity added, the more rapidly is the copper dissolved. If the action has been commenced by a current of nitric oxide gas, the addition of ferrous sulphate, which combines with the gas, arrests it instantaneously. The transmission of oxygen, carbonic acid, or nitrous oxide gas through acid of specific gravity 1·07, or the addition of chloride of lime and carbonates, does not bring about the solution of the metal. If the action has been set up by the addition of nitrite of potassa, it ceases on plunging the vessel into a freezing mixture, when the acid begins to solidify; it recommences, however, as soon as the vessel, by exposure to the air, has attained the temperature of $20°$; a proof that the action caused by the addition of nitric oxide gas or nitrite of potassa is not due to the disengagement of heat. Acid of specific gravity 1·552, which contains rather less than 1 atom of water, does not attack copper at $+20°$; an acid containing from 1 to $4\frac{1}{2}$ atoms of water rapidly dissolves it at $+20°$, but not at $-18°$. When copper is immersed in monohydrated acid at $-18°$, the acid assumes a pale green colour, while the metal becomes covered with a bluish crust, which prevents the further action of the acid, even at $+20°$, and is insoluble in strong nitric acid, but dissolves readily in water. In nitric acid containing 4 or $4\frac{1}{2}$ atoms of water, copper retains its metallic lustre at $-18°$; but on removing the vessel from the freezing mixture, the metal becomes covered with a bluish crust, without any further action taking place, unless the whole is frequently shaken. Nitric acid of specific gravity 1·217 begins to act on copper, even at $-10°$; and acid of 1·108, at $2°$. *Silver* and *mercury* behave like copper. Mercury is completely oxidized by monohydrated nitric acid, even in the freezing mixture, but much more slowly than at a

temperature of 20°, although an insoluble product is formed, probably on account of the mobility of the mercury. In pure dilute nitric acid mercury remains unaltered, unless heat is applied or nitrite of potash added. Silver immersed in rather strong and pure acid becomes covered sometimes with a white, sometimes with a grey crust, which prevents the further action the acid; in nitric acid containing 4½ atoms of water, it dissolves only on the application of heat or the addition of nitrite of potash. (Millon.)

4. Most organic compounds become strongly heated by contact with concentrated nitric acid, frequently even to inflammation, *e. g.*, oil, alcohol, charcoal, &c. The nitric acid is thereby converted into nitric oxide, or frequently into nitrogen gas.

Nitric acid also combines: b. with Peroxide of Hydrogen and Water (p. 78, and *Ann. Chim. Phys.* 8,306; 9,94).

c. With Hyponitric acid and Water.

d. With Hydrochloric acid and Water.

e. With Salifiable Bases it forms a class of salts called *Nitrates, Azotates*, or formerly, *Saltpetres*. These salts are obtained, sometimes by exposing an organic substance mixed with a strong salifiable base to the air (p. 388), sometimes by the direct combination of nitric acid with the base or its carbonate, or with an oxide of a metal formed at the expense of the acid itself. Concentrated nitric acid does not decompose carbonate of soda deprived of its water by fusion, or carbonate of lead, or the carbonates of baryta and lime, even at a boiling heat; doubtless because the nitrates of all these bases are insoluble in strong nitric acid, and the portion of salt first produced protects the remainder by forming a crust around it. Carbonate of potash, on the contrary, is readily decomposed, because the nitrate of potash is soluble in concentrated nitric acid. (Braconnot.) Nitric acid mixed with alcohol does not act on carbonate of potash, and but slowly on carbonate of soda, baryta, or magnesia; the carbonates of strontia and lime, however, are rapidly dissolved by it (Pelouze, *Ann. Chim. Phys.* 50, 434; also *Pogg.* 26, 343); because the nitrates of strontia or lime are readily soluble in alcohol, whereas nitrate of potash is precipitated from its solution in nitric acid on the addition of alcohol. Even hydrate of potash resists the action of nitric acid when mixed with a large quantity of ether, till heat is applied or the mixture shaken. (Braconnot, *Ann. Chim. Phys.* 52, 286; also *Pogg.* 29, 173.) Most of the nitrates have a cooling taste.

All nitrates are decomposed at a red heat: some of them yield tolerably pure oxygen gas at first, and are themselves converted into nitrites: afterwards they give off oxygen gas mixed with nitrogen (*e. g.* nitrate of potash). Others which retain the nitric acid less powerfully, yield oxygen gas and hyponitric acid (*e. g.* nitrate of lead); others again which retain their nitric acid still less forcibly evolve it in an undecomposed form, together with the water which they contain (*e. g.* nitrate of alumina). The base sometimes remains unchanged (as in the lead salt); sometimes it is raised to a higher degree of oxidation (as in the case of manganous nitrate), and sometimes reduced to the metallic state (as with nitrate of silver). Nitrate of ammonia undergoes a still more peculiar change. Combustible bodies both metallic and non-metallic decompose the salts of nitric acid, but in most cases not below a red heat; the decomposition is attended with vivid incandescence and often with explosion, inasmuch as the nitrogen of the nitric acid is disengaged in the gaseous form, and acquires a high degree of elasticity, in consequence of the heat evolved by the union of the oxygen of the nitric acid with the combustible matter.

Such is the case with charcoal, boron, phosphorus, sulphur, iron, zinc, tin, &c. The substance oxidized by the oxygen of the nitric acid frequently unites—at least in part—with the remaining salifiable base. Phosphorus explodes with some of the nitrates, merely on being struck. Tin decomposes some of them even at ordinary temperatures. When sulphuretted hydrogen is passed through a solution of some of the nitrates, as that of baryta, the gas and the nitric acid act upon each other, especially if heat be applied, in such a manner as to produce sulphur, sulphuric acid, and ammonia. (Johnston.)

Hydrochloric acid added in excess to a salt of nitric acid, yields a metallic chloride (or salt of hydrochloric acid) hyponitric acid, and chlorine. (*Scheme* 98.)

$$KO, NO^5 + 2HCl = KCl + 2HO + NO^4 + Cl.$$

Hence the salts of nitric acid (and also those of selenic, iodic, bromic, and chloric acid) impart to hydrochloric acid the property of dissolving gold leaf on the application of heat. The nitrates are decomposed at ordinary temperatures by sulphuric acid; at slightly elevated temperatures, by phosphoric, arsenic, and hydrofluoric acid; and at a red heat by boracic, and frequently also by silicic acid, the base, in all these cases, entering into combination with the decomposing acid. Hence powdered nitrates mixed with oil of vitriol give out a smell of nitric acid; and when heated with powdered bisulphate of potash, evolve yellowish red vapours. Mixed with copper turnings and heated with moderately dilute sulphuric acid, they form a greenish blue solution, and evolve nitric oxide gas, which produces yellowish red fumes of hyponitric acid by contact with the atmospheric air contained in the vessel. When a concentrated solution of a nitrate is mixed with ten times its volume of oil of vitriol, then cooled, and mixed or covered with a strong solution of ferrous sulphate, it assumes at the surface of contact, a rose, purple, violet, or blackish brown colour, according to the quantity of nitrate present; the merest traces of the latter are, however, sufficient to produce a red tinge. (Desbassins de Richemont, *J. Chim. Méd.* 11, 11, 507; Wackenroder, *Ann. Pharm.* 18, 158.) The solution of a nitrate mixed with oil of vitriol and a small quantity of tincture of sulphate of indigo, changes the blue colour of the latter to yellow. This effect is produced when the nitric acid amounts to no more than $\frac{1}{240}$ of the solution; and if common salt be added, $\frac{1}{500}$ of nitric acid is sufficient to produce it. (Liebig, *Schw.* 49, 257.) A strip of paper moistened with the indigo solution, may also be held in the mouth of the tube in which the mixture of nitrate and oil of vitriol is heated. (Chlorates and other salts of similar composition likewise decolorize indigo under these circumstances. An aqueous solution of a nitrate mixed with tincture of litmus and then with oil of vitriol, reddens the litmus without discharging its colour, unless a metallic chloride is present in considerable quantity (this character distinguishes the nitrates from the chlorates). (Vogel, Jun. *J. pr. Chem.* 23, 507.) When oil of vitriol (3 grammes) is mixed with a few drops of the solution of a nitrate, and the liquid stirred up with a small quantity of powdered brucine, a blood-red colour is produced, gradually changing into yellow; in this manner, 1 part of nitric acid may be detected in 10,000 parts of a solution. Narcotine forms an equally delicate test, but the yellow colour precedes the red, which latter is more permanent. (Berthemot, *J. Pharm.* 27, 560.) When a powdered nitrate is introduced into the solution of a few grains of narcotine in 10 drops of oil of vitriol, the salt becomes surrounded with a red ring; but chlorates and similar salts give the same red colour. (Mialhe, *J. Pharm.* 22, 585.)

All nitrates excepting those which are basic, are soluble in water.

f. With certain organic substances.

Fuming Nitric acid, Nitrous acid, Salpetrige Salpetersäure. Spiritus nitri fumans.—Properly speaking, a mixture of nitric acid containing but a small quantity of water with hyponitric acid. Formed by mixing hyponitric acid with concentrated nitric acid, or by passing nitric oxide gas through the latter. According to Mitscherlich, (*Pogg.* 18, 157) 2 parts of monohydrated nitric acid dissolve 1 part of hyponitric acid. It is obtained in the concentrated state, by distilling 2 parts (2 atoms) of nitre with 1 part (1 atom) of oil of vitriol, or with a rather larger quantity of fuming oil of vitriol; also, according to Mitscherlich, by distilling nitre with bisulphate of potassa. When 2 atoms of nitre and 1 atom of oil of vitriol are distilled together, half the nitric acid passes over first, in the form of hydrate; afterwards the other half, at a temperature nearly approaching to redness, and for the most part, decomposed into oxygen gas and hyponitric acid vapour. The latter is absorbed by the nitric acid in the receiver, while the oxygen escapes (see page 391). If the apparatus were tightly connected an explosion would ensue.

Yellowish red liquid, emitting fumes of the yellowish red colour of hyponitric acid but darker; specific gravity = 1·536; solidifies at − 49° (−56° F.) to a very dark red mass.

When it is partially distilled and the product collected in a receiver surrounded with a freezing mixture, two strata of liquid condense in the receiver; the upper of these is hyponitric acid; the lower, unaltered fuming nitric acid; they do not mix when shaken up together. (Mitscherlich, *Pogg.* 15, 618.) A small quantity of water changes the colour of fuming nitric acid to olive green, and causes an evolution of nitric oxide gas; a larger quantity changes it to pale blue; and a still further addition, renders it colourless. On the addition of oil of vitriol to the colourless liquid, these colours re-appear (according to Gay-Lussac,) in the reverse order. An alkali added to fuming nitric acid forms a nitrate, and probably also a nitrite, with evolution of nitric oxide gas. The fuming acid has a much stronger tendency to give up oxygen to other substances, with disengagement of heat and light, than pure nitric acid of an equal degree of concentration.

APPENDIX.

Atmospheric Air.

Since atmospheric air—for reasons already given (I., 20, 22) must be regarded merely as a mixture of oxygen, nitrogen, and other gases, and not as a chemical compound, its examination belongs rather to Meteorology and Analytical Chemistry (since mixtures of elastic fluids can be separated only by chemical means) than to Pure Chemistry.

Properties. Colourless. One litre of air free from aqueous vapour and carbonic acid, weighs at 0° C. and 0·76^{m} Bar., 1·2991 grm. according to Biot & Arago, and 1·2995 grm. according to Dumas & Boussingault.* Now as 1 litre of water at +4° (the point of its greatest density) weighs 1000 grammes, atmospheric air at a temperature of 0° and under a pressure of 0·76 met. must be 770 times lighter than water at + 4°

* 100 cubic inches of air at 32° F. and 29·92 Bar. weigh 32·58864 grains; at 60° F., 30·82926 gr. *Regnault.* (Vid. *Graham's Chemistry. New Ed.* p. 324.)

(*vid.*, L, 281.) In the mass, it probably has a blue colour; it is tasteless and inodorous; adapted for respiration and a supporter of combustion.

Composition. The air is a mixture of nitrogen gas and oxygen gases in almost invariable proportions; small and variable quantities of carbonic acid gas and aqueous vapour are also present; and sometimes also certain other substances, organic and inorganic.

Nitrogen and Oxygen gases. That department of analytical chemistry which teaches the mode of estimating the oxygen present in the air, is called *Eudiometry* (*Luftgüteprüfungs-Lehre*),—because it was at one time erroneously supposed that the salubrity of the air depends upon the amount of oxygen which it contains. Instruments for determining the quantity of oxygen in the air are called *Eudiometers* (*Luftgütemesser.*) In these instruments, the air is, by means of various substances, deprived of its oxygen; and from the diminution of volume thus effected or from the loss of weight sustained, the proportion between the nitrogen and oxygen gases is calculated.

1. *Eudiometer of Dumas & Boussingault.*—A small glass globe is exhausted by the air-pump, weighed, and screwed on to a glass tube likewise weighed and exhausted of air, and containing copper reduced from the oxide by hydrogen gas. The tube is then heated to redness, and the stopcock attached to the outer end of it opened, so that the external air (previously passed over hydrate of potash and oil of vitriol to free it from carbonic acid and water) may enter. Upon this, the other stopcock attached to the tube is opened and also that of the glass globe: the nitrogen of the air then rapidly enters the globe, while the oxygen is completely absorbed by the ignited copper. The three stopcocks are then closed, the tube unscrewed from the glass globe, and both globe and tube weighed,—after which they are again exhausted and reweighed. The difference in weight of the tube and globe before and after exhaustion gives the quantity of nitrogen gas; the increase in weight of the tube, from the oxidiation of the copper contained in it gives the amount of oxygen which was mixed with the nitrogen. (Dumas & Boussingault, *Compt. Rend.* 12, 1005; also *Ann. Chim. Phys.* 78, 257; also *Pogg.* 53, 391.)

2. *Brunner's Eudiometer.*—A tube 3 feet long is half filled with slaked lime and half with asbestos moistened with oil of vitriol, to remove the carbonic acid and moisture from the air which passes through; one end of the tube is open for the admission of air; the other is connected with a second tube. The latter where it enters the first tube is narrow, and then increases to 4½ lines in width for a space of 4 inches,—beyond which is another narrow part about 6 inches in length. This end and half of the broad part of the tube adjoining it is filled with carded cotton wool freed from all moisture by warming and exhaustion. Into the other half of the broad part of the tube adjoining the first tube, a gramme of perfectly dry phosphorus is introduced, together with some asbestos, for the purpose of diffusing the current of air, so that every part of it may come in contact with the phosphorus. The phosphorus is then heated till it fuses, and spread over the surface of the tube by turning the latter about. This tube is then connected on its phosphorus side with the first tube, and on the cotton-wool side with an aspirator containing oil; the phosphorus is heated till it liquefies, and about 4oz. of oil are allowed to escape from the aspirator. In this manner, the cotton wool becomes saturated with phosphorous acid, the use of which is to remove every trace of oxygen from the air in the subsequent experiment. The aspirator is then closed; the second tube weighed, and again con-

nected with the first tube and the aspirator; and the experiment proceeded with by warming the phosphorus, keeping cool the portion of the tube containing the cotton-wool by means of wet filtering paper, and allowing the oil to flow from the vessel merely drop by drop. The volume of the oil which runs out gives directly the volume of the nitrogen which enters the aspirator; the increase in weight of the second tube shows the weight of the oxygen absorbed by the phosphorus; and from the weight, the volume of that element is calculated. In his first experiments, Brunner employed heated iron instead of phosphorus. (Brunner, *Pogg.* 27, 1; 31, 1; also *Ann. Chim. Phys.* 78, 305.)

3. *Saussure's Eudiometer.*—Into a globe of the capacity of about 200 cubic centimetres, and fitted with a metallic screw, leaden shot (about 80 or 100 to the gramme) moistened with about $\frac{1}{17}$ of their weight of water, are introduced. The whole is then shaken with the enclosed atmospheric air, for a space of three hours, till the yellow oxide of lead first formed becomes grey from admixture of metallic lead. The globe is then brought to its original temperature, and opened under water: the volume of the water which enters gives the volume of the oxygen and also of the carbonic acid absorbed; that of the nitrogen is obtained by direct measurement. (Saussure, *N. Bibl. Univers.* 2, 170; also *Pogg.* 38, 171; *Ann. Pharm.* 19, 51.)

4. *Gay-Lussac's Eudiometer.*—Into the atmospheric air to be examined, a copper plate moistened with dilute sulphuric acid is introduced,—which if the acid is from time to time renewed, absorbs the whole of the oxygen gas in the course of a few hours. (Gay-Lussac, *Ann. Chim. Phys.* 62, 219.)

5. *Eudiometer of Berthollet, Parrot.*—The oxygen is removed from a known volume of air contained in a vessel, by allowing phosphorus to burn slowly in it, till the phosphorus ceases to emit vapour and no longer appears luminous in the dark. The residual gas is nitrogen. (Berthollet, *J. Polytechn.* 3, 274; also *Scher. J.* 4, 588; Parrot, *Gilb.* 10, 198; Böckmann, *Gilb.* 11, 61.)—Berthollet (*Statique Chem.* 1, 514) supposed that the residual nitrogen gas expands by $\frac{1}{40}$ of its volume, from absorption of phosphorus; and consequently that this amount ought to be subtracted from the observed volume; but according to Brunner (*Pogg.* 31, 2) the quantity of vapour evolved by phosphorus at ordinary temperatures is too small to cause any perceptible expansion of the nitrogen. If a gaseous mixture to be tested for oxygen, contains any of those gases or vapours which prevent the slow combustion of phosphorus (p. 116) this method is inapplicable. (Graham, *Schw.* 57, 235.) The presence of aqueous solution of potash (which may have been used to remove carbonic acid) also interferes with the action; because the potash, by contact with the phosphorus, disengages phosphuretted hydrogen gas. (Viola, *J. Pharm.* 13, 102.)

6. *Eudiometer of Achard, Reboul, and Seguin.*—Atmospheric air enclosed in a vessel is robbed of its oxygen by phosphorus in a state of rapid combustion: thus, a piece of phosphorus is introduced into an inverted glass tube filled with mercury; and while the phosphorus is heated by a live coal held near the tube, a measured quantity of atmospheric air is suffered to enter the tube in separate bubbles; the tube is then left to cool, and the volume of the residual nitrogen is read off. Any apparatus in which the burning phosphorus comes in contact with the whole of the air at once, is very apt to break. (Achard's *Physik. Chem. Abhandl.* 1, 327; Reboul, *Ann. Chim.* 13, 38; Seguin, *Ann. Chim.* 9, 293; also *Crell. Ann.* 1794, 2, 453; Bischof, *Schw.* 37, 168.)

7. *Eudiometer of Scheele and De Marty.*—The oxygen gas is removed from atmospheric air by agitating it for a quarter or half an hour, with an aqueous solution of monosulphide or polysulphide of potassium, or pentasulphide of calcium (obtained by boiling sulphur with lime and water). The solution must be prepared cold; or, if heat is applied in its preparation,—whereby the nitrogen gas absorbed from the air is expelled—it must be shaken up when cold with atmospheric air, in order resaturate it with nitrogen; if this precaution be not taken, the liquid will absorb nitrogen from the air to be analyzed. The diminution of volume gives the exact amount of oxygen. (Scheele, *on Air and Fire,* 64; De Marty, *Scher. J.* 8. 63; also *Gilb.* 19, 389; *N. Gehl.* 4, 146; and *Gilb.* 28, 422; Guyton Morveau, *J. Polytechn.* 2, 166; Von Humboldt & Gay-Lussac, *Gilb.* 20, 42; Hope, *Gilb.* 19, 385.)

8. *Volta's Eudiometer.*—To a measured quantity of atmospheric air contained in a detonating tube standing over water or mercury, a measured quantity of pure hydrogen gas is added (amounting to at least half and not exceeding the whole volume of the air,) and the mixture exploded by the electric spark. The gaseous residue, consisting of the whole of the nitrogen and the excess of hydrogen, is then measured, and its volume deducted from the original volume of the air + that of the hydrogen gas before explosion; the difference divided by 3 gives the volume of oxygen that was present in the air under examination. (Volta, *Brugnat. Annali di Chimica,* 1, 171; 2, 161; 3, 36; Humboldt & Gay-Lussac, *A. Gehl.* 5, 45; also *Gilb.* 20, 38: A. Berthollet, *Gilb.* 34, 452: Gay-Lussac, *Ann. Chim. Phys.* 66, 443; also *J. pr. Chem.* 14, 61.) Instead of employing the electric spark, the mixture of atmospheric air and hydrogen may be inflamed by a platinum wire wound into a coil and heated to redness by a galvanic battery. (Grove, *Phil. Mag. J.* 19, 99.) The mixture may also be made to combine slowly by means of finely divided platinum; this method is best adapted for gaseous mixtures containing extremely small quantities of oxygen, and therefore not capable of being exploded by the electric spark. It has also the advantage of not condensing any nitrogen gas in the form of ammonia, which is the case when the mixture is exploded. For this purpose, balls made of platinum and clay (p. 49), introduced into the mixture on a platinum wire answer very well; or spongy platinum placed in a small inverted capsule and introduced by means of a platinum wire, so that it may not get wet; or the measured mixture of gases may be introduced into a tube, the surface of which is covered with finely divided platinum. (Döbereiner, *Gilb.* 74, 272; *Schw.* 47, 122; *Kastn. Arch.* 9, 341; *J. pr Chem.* 15, 284; Pleischl, *Schw.* 39, 150 & 204; Turner, *Ed. Phil. J.* 11, 99; also *Pogg.* 2, 210; Degen, *Pogg.* 27, 557.)

9. *Fontana's Eudiometer.*—First used by Priestley.—100 measures of atmospheric air contained in a graduated tube standing over water are mixed with 100 measures of nitric oxide, and the diminution of volume observed. Out of 200 measures of the mixture, between 80 and 90 measures generally disappear. It must be observed, however, that nitric oxide is capable of uniting with oxygen in different proportions, inasmuch as 4 measures of nitric oxide with 1 measure of oxygen form nitrous acid; with 2 measures, hyponitric acid; and with 3 measures, nitric acid. Moreover, one or other of these compounds will predominate, accordingly as the excess of the nitric oxide over the oxygen is greater or smaller—or as the atmospheric air or the nitric oxide enters first into the tube—or according to the rapidity with which the two gases are mixed—the width

of the tube—the agitation or quiescence of the mixture—the temperature, &c., &c. Consequently, this form of eudiometer, notwithstanding the improvements that have been made in it, is the least accurate of all; and, in former years, when it was used in preference to all others, gave rise to very inaccurate statements respecting the amount of oxygen contained in the air, which was said to vary considerably according to the direction of the wind, the season of the year, the salubrity of the atmosphere, &c. According to Scherer, $\frac{1}{3}$ of the diminution of volume should be regarded as oxygen gas; according to Ingenhouss, $\frac{10}{48}$; according to Gay-Lussac, $\frac{1}{4}$, provided the mixture is contained in a large vessel and not shaken; according to Von Humboldt, $\frac{10}{36}$; according to Lavoisier, from $\frac{100}{273}$ to $\frac{100}{383}$; according to Priestley, $\frac{100}{379}$; according to Hildebrandt, $\frac{1}{3}$; and according to Dalton, from $\frac{1000}{2714}$ to $\frac{1000}{4428}$. (*Vid.* Fontana, *Descrizione ed usi di alcuni strumenti per misurare la salubrità dell' aria. Firenze*, 1770 :—Ingenhouss, *Crell. Chem. J.* 1, 215 :—Lavoisier, *Crell. Ann.* 1788, 2, 426 :—Cavendish, *An Account of a New Eudiometer, Lond.* 1783; also *Phil. Transact.* 1783:—Von Humboldt, *Versuch einer Zerlegung des Luftkreises;* also *Scher. J.* 1, 263; 3, 88 & 146:—Dalton, *Gilb.* 27, 369:—Gay-Lussac, *N. Gehl.* 9, 445; also *Gibl.* 36, 37.)

10. *Sir H. Davy's Eudiometer.*—A solution of ferrous sulphate saturated with nitric oxide gas serves for the absorption of oxygen gas; but as a portion of nitric oxide from the solution readily mixes with the residual nitrogen gas, the former must be removed by agitation with a pure solution of ferrous sulphate. (H. Davy, *Gilb.* 19, 394.) As the liquid also evolves a small quantity of nitrogen, proceeding from the decomposition of the nitric oxide, this method gives the proportion of nitrogen too high. (Berzelius.)

[On Eudiometers in general, *vid.* Dalton, *Phil. Mag. J.* 1258; also Regnault & Reiset, *N. Ann. Chim. Phys.* 26, 299.]

In those methods which require a considerable lapse of time, so that the temperature and atmospheric pressure may vary during their performance, the necessary corrections must be made.

From the experiments of Dumas & Boussingault, Brunner, and other chemists, it may be considered as established that atmospheric air freed from carbonic acid and aqueous vapour contains in 100 parts by weight, 23 parts of oxygen and 77 parts of nitrogen,—and in 100 volumes, 20·8 volumes of oxygen gas and 79·2 volumes of nitrogen gas; and that these proportions undergo but very little variation, never amounting to 1 per cent. Differences of years, seasons, winds, weather, locality, and height and salubrity of the atmosphere, have little or no influence. A great part of the variations obtained by individual chemists may be attributed to the use of defective methods, or to errors of observation.

¶ From the late experiments of Regnault & Reiset (at Paris), it appears that 100 volumes of air contain, on the average, 20·96 volumes of oxygen gas. (*Compt. Rend.* 26, 4; also *Ann. Pharm.* 68, 221.) ¶

Dumas & Boussingault (*Compt. Rend.* 12, 1005; also *Ann. Chim. Phys.* 78, 257; also *Ann. Chim. Phys.* 78, 291), found, in the year 1841, in 100 parts by weight of air taken from the Jardin des Plantes at Paris, and freed from aqueous vapour and carbonic acid, the following proportions of oxygen; annexed, are also the quantities of oxygen found on the same days by Brunner in the air at Bern, and by Martins & Bravais in the air on the Faulhorn, 2683 metres or 8803 feet above the sea-level :

	Barometer.	Temperature.	Wind.	Weather.	Paris.	Bern.	Faulhorn.
27 April	0·7595 M.	23°	S	Fine	22·92		
28 ——	0·7583 „	25°	SE	Fine	23·06		
29 ——	0·7576 „	27°	NE	Fine	23·03		
29 May	0·7579 „	17·4°	N	Rain	23·01		
20 July	0·7339 „	19°	S	Rain	23·00	23·00	22·96
21 ——	0·7520 „	14·7°	SW	Fine	23·00	22·89	23·09
24 ——	0·7582 „	17·8°	NNW	Cloudy	23·08	22·97	22·91
20 September	0·7589 „	22·6°	N	Fine	23·07	7 August	22·97
22 ———	0·7512 „	21°	SSW	Cloudy	22·89		
Mean of the quantity of oxygen in 100 parts by weight of air					23·07		

Verver found in the air at Groningen 22·998 parts by weight of oxygen;—Marignac (*Compt. Rend.* 14, 379), in that of Geneva, 22·98 parts;—Levy found in the land air at Copenhagen 22·998 parts; in the sea air taken just above the surface of the sea, 22,575 parts; in the sea air, 35 feet above the level of the sea, 23·016 parts; so that the air near the surface of the sea is poorer in oxygen.—Stas (*Compt. Rend.* 14, 570) obtained (at Brussels?) in 12 experiments, from 23·04 to 23·08 parts; but in an experiment performed at a different time with an equal degree of care, 23·11, and in another, 23·14 parts of oxygen.

Berthollet (*Gilb.* 5, 349) found in 100 measures of atmospheric air, at Cairo and at Paris, nearly 22 measures of oxygen gas;—Saussure found at Geneva (*Gilb.* 1, 508) from 21 to 22 measures, and in his more recent experiments with eudiometer (3), 20·6 measures;—De Marty (*Gilb.* 19, 389) found in the air in Catalonia, with every kind of wind and weather, under various degrees of atmospheric pressure, and at every season of the year, also over morasses and stagnant pools, and in places where large assemblies of people were collected—from 21 to somewhat less than 22 measures; Sir H. Davy (*Gilb.* 19, 394) found in the air at Bristol and other parts of England, also in air taken from over the sea on the west coast of England during a west wind, and in air brought from the coast of Guinea, 21 measures of oxygen gas;—Berger (*Gilb.* 19, 412) found the air on the Jura, on the mountains and in the valleys of Savoy, on the glaciers in that locality, and in the Valais, to contain from 20·3 to 21·65 measures;—Configliachi (*Schw.* 1, 144), found on the Simplon, Mount Cenis, and other mountains of the Alps, 21; over swampy meadows, 21; over rice-fields, 20·8; and in close places, 20·3 volumes;—Gay-Lussac & Von Humboldt at Paris, in every kind of weather and season of the year, found from 20·9 to 21·1 volumes; Gay-Lussac (*Gilb.* 20, 33), 6636 metres or 21,772 feet above the surface of the earth, and likewise in Paris, 21·49 volumes;—A. Vogel & Krüger (*Gilb.* 66, 94), over the Baltic Sea, 20·59 volumes;—Hermbstädt (*Schw.* 32, 281) found in the month of April, on the shore of the Baltic, 5 feet above the sea-level, 21·5; and at 16 feet above, 20·5 volumes, while the air over the land contained 20 volumes of oxygen (from which he concludes that sea-water gives off oxygen gas);—Dalton (*Ann. Phil.* 26, 304) found in England, generally from 20·7 to 20·8, more rarely 21; and on the 8th of January, 1825, at 30·9 in. atmospheric pressure, and with a north-east wind, the maximum, viz., 21·15 volumes. From the following more recent observations, in which atmospheric air, taken at the same time from an elevated and a low locality, was examined, Dalton (*Phil. Mag. J.* 12, 397) concludes that the air in elevated regions contains rather less oxygen gas than that nearer the level of the sea. From the constant intermixture

however of the air by winds, &c., the difference in amount of oxygen cannot be so great as it should be in accordance with his theory (I. 22, 2). Air from Helvellyn (3000 feet high), contained 20·64 volumes; from Manchester, 20·99 volumes of oxygen gas; also from Helvellyn, 20·63; from Manchester, 20·73; air from Snowdon (3570 feet high), 20·70; from the level country three English miles from Manchester, 20·85; air collected by Grafton in a balloon 9600 feet above the level of the sea, 20·70; from Manchester, 20·83. Air collected by Green in a balloon 15,000 feet high, 20·62; from Manchester, 20·95; air from the Mer de Glace near Chamounix, 6000 feet high, 19·80; from the Simplon, 6174 feet in height, 19·76; from the Wengern Alp, 6230 feet high, 20·28 volumes.—Th. Thomson (*J. pr. Chem.* 8, 365) found in the air at Glasgow, as a mean of a great many experiments, 21·01 volumes of oxygen gas;—Kupffer (*Schw.* 57, 214) found in the air at Kasan from 21 to 21·2 volumes;—Brunner (*Pogg.* 31, 7,) found in Switzerland during the month of July, in the open country, 21·0705, and according to his more recent experiments (*Ann. Chim. Phys.* 78, 305), 20·85 volumes; on the Faulhorn, 20·915 volumes.—Boussingault, (*Ann. Chim. Phys.* 76, 360) found at Mariquita, 548 metres or 1799 feet above the sea-level in November, 20·77; at Ibaqué, 1323 metres or 4341 feet high, in December, 20·7; and at Santa Fé de Bogota, 2643 metres or 8671 feet high, during April, 20·65 volumes.—Air taken by Green, by means of his balloon, at an elevation of 11,300 feet, contained 21 volumes.—Baumgartner (*Medic. Jahrb. d. öster Staats*, 12, 83), in Vienna, during the cholera, found from 20·4 to 21·4 volumes of oxygen gas in 100 volumes of air.

In a coal-mine on the Ruhr, Bischof (*Schw.* 39, 285,) found 22·93 volumes of oxygen gas, whilst the air on the outside contained only 21·35 volumes.

In the air which escapes from fissures in glaciers, Bischof (*Schw.* 37, 266) found only 10·22 volumes of oxygen gas to 89·78 volumes of nitrogen, because the water formed from the melting ice absorbs proportionally more oxygen than nitrogen from the air (p. 67). In the same manner, Saussure and Senebier found that atmospheric air liberated from the snow of the Alps by thawing, was poor in oxygen. A similar result was obtained by Boussingault (*Ann. Chim. Phys.* 76, 354) with snow from the Andes and from Paris. On melting the snow in an inverted bottle completely filled with it, the air which rose to the top was found to contain—that from the Andes, from 16 to 17 volumes, and that from Paris, 18·7 volumes of oxygen; the resulting snow-water, when boiled, yielded bubbles of air containing 32 volumes of oxygen gas, a proof that it had absorbed the oxygen gas in preference to the nitrogen of the air. If however a bottle be filled with snow, and the air which it contains pumped out, it is found to contain from 20 to 21 volumes of oxygen gas. If the snow be lightly pressed into a vessel, the air contained in the vessel after the liquefaction of the snow contains, according to Lampadius, (*J. pr. Chem.* 10, 78) 19·71 volumes; but if the snow be closely pressed down, only 18·91 volumes of oxygen gas. 1000 of snow-water obtained from snow fallen during a west wind yield, when boiled, 33·31 volumes of atmospheric air, which in 100 volumes contain 68·85 volumes of nitrogen gas, 30·12 of oxygen, and 10·3 volumes of carbonic acid gas. If the snow be closely pressed into a vessel, and the greater part of the air removed from it by moistening with cold boiled water, the resulting snow-water, when boiled, yields only $\frac{1}{3}$ as much air, because on liquefying, it finds but a small quantity of air to absorb.

Carbonic acid gas. Formerly the amount of carbonic acid in the air was estimated by the diminution in volume observed on agitating it with aqueous solution of ammonia, potassa, baryta, or lime, in Humboldt's *Anthracometer* for example. (Gilb. 3, 77.) But as the quantity of carbonic acid in the air is very small, the results obtained by this method were inaccurate and the amount of carbonic acid was generally estimated too high.

Thénard introduces a small quantity of baryta water into atmospheric air contained in a glass globe of the capacity of 10 litres and furnished with a stop cock, and agitates till the whole of the carbonic acid is absorbed; he then exhausts the globe, and allows a second quantity of air to enter,—agitates and again exhausts,—and so on, till the baryta-water has been treated thirty times with fresh portions of air. The weight of the precipitated carbonate of baryta is then obtained, and from it is calculated the volume of carbonic acid gas contained in the volume of air employed. Saussure (*Ann. Chim. Phys.* 2, 199; also *Gilb.* 54, 217; —*Ann. Chim. Phys.* 3, 170;—*Ann. Chim. Phys.* 44, 5; also *Bibl. Univ.* 44, 23 & 138; also *Schw.* 60, 17 & 129; also *Pogg.* 19, 391) at first employed a method similar to that of Thénard's; subsequently he exhausted a vessel capable of holding 30 litres; suffered the air under examination to enter; agitated the mixture; poured in the baryta-water; and determined the amount of the carbonate of baryta thrown down.

Brunner (*Pogg.* 24, 569; *Ann. Chim. Phys.* 78, 305), by means of an aspirator, draws the air to be examined, first through a tube containing asbestos moistened with oil of vitriol, to render it anhydrous, and then through a second tube, which is first narrow for a short distance, then wide for a considerable length, and then narrow for a still greater length. This tube contains hydrate of lime in the wide part, to absorb the carbonic acid; and in the long narrow portion, asbestos moistened with oil of vitriol, to retain the water which the air reabsorbs from the hydrate of lime. The increase in weight of this tube gives the quantity of carbonic acid contained in the air which passes through it; and the volume of water from the aspirator, added to the calculated volume of the carbonic acid gas obtained, gives the original volume of the air examined.

According to the experiments of Saussure and Brunner, which agree, 100 volumes of inland air may be regarded as containing, on an average, 0·05 vol. of carbonic acid gas.

Saussure examined the air over a meadow at Chambeisy, three-quarters of a mile from Geneva, 250 metres from the Lake of Geneva, 16 metres above the lake, and 388 metres above the sea-level. In dry months, 100 volumes of air contained from 0·0479 to 0·0518 vol. of carbonic acid gas; after long rains, from 0·0357 to 0·0456 vol.; in December, when the ground was damp, and the weather cloudy, from 0·0385 to 0·0425 vol.; in January, during a frost, 0·0457 vol.; at the end of January, with frequent thaws, 0·0427 vol. Hence it appears that moisture on the ground diminishes the amount of carbonic acid in the air by absorption; frost prevents the absorption. The air over the Lake of Geneva contained 0·0439 vol., whilst at the same time the air of the meadows contained 0·046 vol. The air at Geneva contained 0·0468, whilst that from the meadow contained 0·0457 vol. The air on the mountains contained more carbonic acid than that of the meadows, the difference amounting to 0·0557 vol., probably because the air in the upper regions meets with fewer plants and less moist ground, by which the carbonic acid [driven upwards by the processes of combustion]

can be absorbed. The quantity of carbonic acid in the air during a light wind, is to the quantity during a gale, on the average, as 0·0376 : 0·0398, because a strong wind mingles the higher strata of air with the lower. The mean proportion of carbonic acid in summer at noon is to that at night as 0·0398 : 0·0432; in winter the difference is less, and sometimes disappears entirely, though it has frequently been found to exist even when the earth has been covered with snow, at a temperature below 0°. The maximum quantity of carbonic acid was found at the end of night, the minimum at the close of day. The quantity of carbonic acid was greatest during the nights as compared with the days, during a thaw, with the temperature much lower at night than in the day time. During high winds, no difference was observed between the quantity of carbonic acid by night and by day. (Saussure.)

Watson (*J. pr. Chem.* 6, 75) found in 100 volumes of air, at Bolton, a mean of 0·053 vol., and in air obtained, at a distance of six miles from Bolton, a mean of 0·04135 vol. of carbonic acid; and less when the wind blew from the sea than when it blew from the land.

Dalton estimated the amount of carbonic acid in 100 volumes of air at 0·065; Configliachi, at 0·08; Von Humboldt, at 0·5—1·8 vol.

Carbonic acid gas is also present in the air on Mont Blanc (Saussure), and according to Beauvais is as abundant in air collected by means of a balloon 650 toises above Paris as in the air of Paris itself.

On the contrary, the air over the sea is found to contain sometimes a much smaller quantity of carbonic acid and sometimes none at all. The air over the Baltic at Doberan, and over the North Sea at Dieppe contains scarcely any carbonic acid. (A. Vogel.) At Rostock, the air does not render lime water turbid when the wind blows from the north (the direction of the Baltic); but that effect is produced when the south wind blows (which comes from the land). (Krüger, *Schw.* 35, 379.) Emmet, however, (*Phil. Mag. J.* 11, 225) found carbonic acid in the sea-air throughout his whole voyage from North America to Bermuda; and at Bermuda, 100 volumes of air were found to contain 0·0125 vol. of carbonic acid gas.

In close rooms, in which the oxygen of the air is vitiated and carbonic acid produced by the processes of respiration and combustion, the atmosphere would soon become unfit to breathe, were it not for the change of air which takes place through the crevices of the doors and windows, or which is produced by artificial ventilation. (See the researches of Leblanc, *Compt. Rend.* 14, 862.) [On the air in the mines of Cornwall, which contains, on the average, 82·848 volumes of nitrogen, 17·067 volumes of oxygen, and 0·085 vol. of carbonic acid. *vid.* Moyle, *Phil. Mag. J.* 19, 356.]

Vapour of Water.—Estimated either by the *Hygrometer* and *Psychrometer* (I., 274, 275, and 289), or more correctly by the method of Brunner (*Ann. Chim. Phys.* 78, 305), in which the air is drawn by means of an aspirator through a tube containing asbestos slightly moistened with oil of vitriol, and its increase in weight determined.

The quantity of aqueous vapour in the atmosphere is extremely variable, and is greater in Germany, during southerly and westerly winds in summer and hot weather, than during northerly and easterly winds in winter and in cold weather.

Other Inorganic Matters in the Air.—These must be regarded as acci-

dental impurities, sometimes produced by atmospheric electricity, sometimes rising in the form of vapour from peculiar spots on the earth's surface, or carried by the wind in the form of dust from the land or from the sea to the higher regions of the atmosphere. They are chiefly found in rain water, especially in that which falls after a long drought. The following substances have been thus found:—*Hydrosulphuric, sulphuric, hydrochloric, and nitric acids; ammonia, potash, soda, lime, magnesia, iron, manganese,* &c.

Hydrosulphuric acid.—At Amsterdam, evolved from materials containing gypsum used for burning; partly converted into *sulphuric* acid. (Von Driessen & Veehof.) Hydrosulphuric acid is also found in the air over sulphurous springs, and over particular parts of the sea (see p. 191.)

Sulphurous acid with small quantities of *sulphuric acid.*—Found in the air of London (from the combustion of coal); the air and the rain water of London consequently redden litmus. (Darcet, Chevallier, *J. pr. Chem. Med.* 10, 292.)

Hydrochloric acid: Found on the coast during a sea-breeze. (A. Vogel, *Gilb.* 66, 97; 72, 278;—Von Driessen, *Schw.* 36, 139.)—Roubaudi *J. Pharm.* 19, 569; 21, 141) filled a glass globe with a freezing mixture, exposed it on the coast at Nizza, from 6 to 50 paces from the shore, and examined the water condensed on the globe. During a calm, or even with a rough sea and no wind, it behaved like distilled water, but with a boisterous sea and a sea-breeze, the water contained hydrochloric acid and all the other ingredients of sea-water. The same results were obtained on employing Brunner's aspirator. Hydrochloric acid and the other components of sea-water do not therefore rise in vapour from the sea; but the sea-water itself, during a high wind, is diffused in fine particles through the air. Rain or snow which fell at Freiberg, while the air was tranquil, and after a previous fall of rain or snow, yielded no residue on evaporation; that which fell during a strong west wind contained salts, especially chloride of calcium. (Lampadius, *J. pr. Chem.* 13, 244.)—Meissner, (*Schw.* 36, 161) did not find any hydrochloric acid in the air of Halle near the salt works.—All the rain-water which fell at Giessen, at 77 different times during a period of two years, was found to contain common salt. (Liebig, *Ann. Chim. Phys.* 35, 320.)

Nitric acid: Appears to have been first observed by Priestley. Of the above mentioned 77 different specimens of rain-water, 17 were obtained during thunder-storms; in the latter, nitric acid was found combined with ammonia and lime; of the remaining 60, two only contained a trace of nitric acid: so that lightning in passing through the air, forms nitric acid. (Liebig.) In tropical regions, electrical discharges are constantly taking place in the clouds; and this is probably the origin of a great portion of the nitric acid which is found on the surface of the earth in the form of nitre. Boussingault (*Ann. Chim. Phys.* 57, 179) and Lampadius also (*J. pr. Chem.* 14, 54) found that rain-water collected after a severe thunder-storm reddened litmus and contained 0·3 grains of nitric acid in a pound.

Ammonia: Probably disengaged, in union with carbonic or other acids, from azotized organic matter undergoing the process of putrefaction or combustion. Scheele (*Opusc.* 2, 373) found that ammoniacal salts collected round the mouths of bottles containing hydrochloric or sulphuric acid, when kept in a room.—Saussure (*A. Gehl.* 4, 691,) observed that sulphate of alumina exposed to the open air, was converted into ammonia-alum.—Dilute sulphuric acid exposed to the open air on a

roof at Paris, was found to contain ammonia. (Collard de Martigny, *J. Chem. Med.* 3, 516.)—White clay heated to redness and then exposed to the air for a week, yields a considerable quantity of ammonia when heated again, which is not the case if it be kept in a close vessel. (Faraday.)—Zimmermann (*Kastn. Arch.* 1, 257) and Brandes (*Schw.* 48, 153.) found a trace of ammoniacal salts in rain-water evaporated to dryness. Zimmermann, however, attributed the ammonia to the decomposition of the organic matter, by heat.—Chevallier (*J. Pharm.* 20, 655) often found a large quantity of ammonia in the air; at Paris, it was sometimes combined with hydrosulphuric acid and acetic acid.—Rain-water or snow collected in the open fields, yields a distillate which contains carbonate of ammonia, and, when evaporated with a small quantity of hydrochloric acid, leaves sal-ammoniac having a yellow or brown colour. An ammoniacal salt is likewise obtained when rain-water is evaporated with sulphuric or nitric acid. (Liebig. *Chemistry, in its Application to Agriculture and Physiology. London*, 1843, p. 45.) Rain-water, deposited during thunder-storms, likewise contains nitrate of ammonia. (Liebig.)

¶. The quantity of ammonia contained in the air has been determined by Gröger. (*Ann. Pharm.* 56, 208, by Kemp, and quite recently by Fresenius, (*N. Ann. Chim. Phys.* 26, 208.) The following table exhibits the results obtained. 1,000,000 parts of air contain:

	Ammonia.	Oxide of Ammonium.	Carbonate of Ammonia.
Gröger	0·333	0·508	0·938
Kemp	3·880	5·610	10·370
Fresenius {day	0·098	0·153	0·283
Fresenius {night	0·169	0·257	0·474
Fresenius (mean)	0·133	0·205	0·379

The results found by Gröger—and still more those obtained by Kemp—are certainly too high. Gröger appears to have neglected to assure himself that the re-agents which he used were perfectly free from ammonia; and Kemp's mode of experimenting (which consisted in passing the air through a solution of corrosive sublimate, then boiling the solution, and determining the ammonia by the quantity of white precipitate so obtained), is not to be depended on. From the experiments of Fresenius, it appears that the quantity of ammonia contained in the air during the day, is to that which is present during the night, as 1 : 1·7. The comparative smallness of the quantity present during the day, may be due to two causes: 1. That in the day-time, more ammonia is expended in the nutrition of plants; 2. That the ammonia which accumulates during the day and night together is dissolved and precipitated by the dew at sunrise. ¶.

When some weeks have passed without a storm, the rain-water contains lime dissolved in excess of carbonic acid. (Stark, *Ann. Phil.* 3, 140.)—In hail stones which fell during the month of February, sulphate of lime was found. (Girardin, *J. Pharm.* 25, 390.)—On evaporating snow-water, sulphate of lime and chloride of calcium remain; water from thunder-showers leaves sulphate of lime. In fetid vapours and mountain mists, phosphoric acid is found. (Wiegmand, *Br. Arch.* 7, 199; 16, 151.)—Rain-water leaves, on evaporation, carbonate and sulphate of lime, chloride of calcium, silica, and a trace of iron. (Bohlig, *Kastn. Arch.* 26, 419.)—All the rain-water that falls at Salzuffeln leaves, on evaporation, a residue which for 10,000,000 parts of water amounts, during May, to

only 8 parts, which is the minimum, but during January, to 65 parts, which is the maximum.

This residue contains an ammoniacal salt, chloride of sodium with a small quantity of chloride of potassium, carbonate and sulphate of lime, carbonate, sulphate, and hydrochlorate of magnesia, the sesquioxides of manganese and iron, a resinous substance, a substance soluble in water and dilute alcohol, and an animal substance, soluble only in potash. (Brandes, *Schw.* 48, 153).—Zimmermann states (*Kastn. Arch.* 1, 257,) that he found in rain-water, carbonic acid, hydrochloric acid, potash, lime, magnesia, manganese, and iron, and sometimes also nickel, accompanied by pyrrhin; (*vid.* seq).—Bertels (*J. pr. Chem.* 26, 89) says that he obtained from 3 pounds of snow-water, as much as 86 grains of anhydrous residue. Unless, however, the evaporation is conducted in metallic retorts, with every precaution to prevent the entrance of ashes and particles of dust, such experiments are not entitled to any great degree of confidence.

Organic Matter in the Atmosphere.—If a bottle filled with distilled water be emptied in the open air either over the land or over the sea, and a small quantity of nitrate of silver solution put into the bottle, the silver salt when exposed to light, becomes first red, then violet, and lastly deposits a dark-coloured precipitate. In a similar manner also, rain and snow-water redden a solution of silver exposed to light. This red colour is not produced by chlorine or hydrosulphuric acid, but by organic matter.—Zimmermann regards this organic matter as a peculiar substance, and names it *Pyrrhin.* But as many organic substances have the property of reddening a solution of silver exposed to light, the supposition of A. Vogel is more probable, that the effect is due sometimes to one, and sometimes to another kind of organic matter, diffused through the air in the form of fine particles or dust. (See Hermbstädt, *Schw.* 32, 281;—Krüger, *Schw.* 33, 379;—Lampadius, *Schw.* 33, 199; *J. pr. Chem.* 10, 78; 13, 244;—Pfaff, *Schw.* 35, 396; 52, 311;—A. Vogel. *Gilb.* 72, 282 & 336; *Kastn. Arch.* 15, 97;—Wiegmann, *Kastn. Arch.* 16, 196;—Braconnot, *Ann. Chim. Phys.* 44, 300:—Roubaudi, *J. Pharm.* 21, 141;—Girardin, *J. Pharm.* 25, 390.)

The red colour produced by rain or snow-water with a solution of silver under the influence of light, is destroyed by chlorine. After long standing, the red mixture (not treated with chlorine) deposits a precipitate which becemes black by exposure to light, and yields carbonate of ammonia by dry distillation. In a garden fragrant with flowers, or in a hot-house, or under a receiver containing odoriferous flowers, a dilute solution of silver becomes red, if exposed at the same time to the sun's rays. A solution of volatile oil in water, alcohol containing fusel oil, distilled vinegar, benzoic acid, a solution of roasted starch, and an aqueous infusion of beech-wood, or peat, produces the same red colour in a solution of silver exposed to light. (A. Vogel.)

Water from hail-stones which fell in February, 1839, presented a milky appearance due to the presence of a small quantity of organic matter, and deposited a few white flakes; when mixed with solution of silver, it remained colourless in the dark, but on exposure to light became first reddish and then brown, and deposited a scanty grey flocculent precipitate, which, on being heated, evolved fumes having an empyreumatic animal odour. When the water was evaporated to dryness by itself, and the residue heated, a similar empyreumatic odour was emitted. The water did not contain ammonia ready formed, but gypsum (p.412). (Girardin.)

Snow-water collected at Freiberg during a westerly wind, immediately becomes turbid on the addition of solution of silver, after which it blackens on exposure to light, because it contains chloride of calcium; snow-water collected at the same place during an east wind, gives scarcely any turbidity, but becomes red when exposed to the sun's rays,—and then deposits a dark-coloured precipitate, from which a boiling solution of common salt removes only the chloride of silver present. The residue burns before the blow-pipe with a faint light and leaves metallic silver. The stronger the wind which blows from the continent the richer is the air in matter which reddens the silver solution. The matter thus conveyed by the wind probably consists of dust from the surface of the ground. (Lampadius.)

Two thousand measures of air freed from every trace of carbonic acid, and exploded with hydrogen gas, yield 0·94 measures of carbonic acid gas; so that the air probably contains carbonic oxide gas [or marsh gas, or some other organic substance]. (Saussure, *Pogg.* 19,431.)

If the air of Paris is first passed through a bottle containing oil of vitriol—then through a long chloride of calcium tube—then through two tubes full of asbestos moistened with oil of vitriol (by the equality in weight of the latter before and after the experiment it is ascertained that the air is previously rendered perfectly dry)—then into a tube containing ignited copper turnings, in which the combination of the hydrogen in the air with the oxygen is effected—and lastly, into a weighed tube containing asbestos moistened with oil of vitriol: the increase in weight of the latter gives the quantity of water produced, and consequently the quantity of hydrogen present in the air, independent of that which is in the form of aqueous vapour. In this manner it is found that 100 parts by weight of air examined on different days, contain from 0·0002 to 0·0008 parts by weight of hydrogen. The latter is probably exists partly as hydrogen gas, partly as hydrosulphuric acid gas (which however would be decomposed in passing through the oil of vitriol), and partly as *marsh gas*. The latter is evolved from every description of stagnant water, from coal mines, and in the processes of combustion; but can accumulate in the atmosphere in small quantities only, because, like free hydrogen, it is consumed by electric discharges in the air. Atmospheric air from a pestilential region in South America, when passed through a chloride of calcium tube into an empty red-hot tube, yielded water, the quantity of which corresponded to 0·0017 of hydrogen in 100 parts by weight of air. When the air has been rendered wholesome by thoroughly draining the morasses, it contains only 0·0004 of hydrogen. If the air is deprived of its aqueous vapour by means of oil of vitriol instead of chloride of calcium, it does not yield any water on being transmitted through the red-hot tube, because the oil of vitriol retains the organic matter in which the hydrogen is present. Oil of vitriol exposed in a watch-glass, rapidly blackens in pestilential localities—for example, in the neighbourhood of a marsh in the Department de l'Ain,—also in Maracey, Valencia, and Cartago in South America, during the unhealthy season. If a watch-glass full of warm water, and an empty watch-glass are exposed at the same time in an unhealthy atmosphere, till the latter is covered with dew, then one drop of oil of vitriol put into each, and the contents of each evaporated to dryness—no residue remains in the first, but a carbonaceous residue in the second,—because the dew charged with miasma could not condense on the former. If the accidental presence of insects or of dust were the

cause of the blackening of the oil of vitriol, both watch-glasses would behave in the same manner with that reagent. (Boussingault, *Ann. Chim. Phys.* 57, 148; also *J. pr. Chem.* 3, 151.)

Moscati (*Gilb.* 43, 12) suspended glass globes filled with ice close over the unhealthy rice-fields of Tuscany. The hoar-frost deposited on them during the night yielded, on thawing, a transparent water which in a short time deposited small flakes of a substance containing nitrogen, and after a while became putrid. Similar results were obtained in an hospital. Water collected by Rigaud de l'Isle on the marshes of Languedoc behaved in a similar manner; with a solution of silver it gave a precipitate which soon became purple. Whether the organic matter condensed with the water was really the miasma, remains undecided. At all events A. Vogel (*J. pr. Chem.* 4,279) by exposing in his lecture-room, immediately after the departure of the audience, glass cylinders filled with a freezing mixture and standing on plates, obtained a transparent water which behaved similarly to the above. After some days, it deposited first white and then green flakes, and acquired a mouldy smell. Mixed in a fresh state with a solution of silver, it remained colourless and transparent in the dark; but on exposure to the sun's rays, assumed a dark port-wine colour in the course of a few minutes, then became colourless, and deposited a black powder. Hence non-contagious organic particles diffused through the atmosphere, may also produce water exhibiting the above characters.

The following circumstances appear to promote the disengagement of miasmata. The putrefaction of organic substances exposed in hot weather to the action of air and moisture. Stagnant waters exhale miasmata, in greatest quantity when they are completely drained and the air is allowed to act on the decomposing organic matter. (Ferguson.) The rotting of flax and hemp under water produces miasma. The clearing of forests in South America renders the surrounding country unhealthy, in consequence of the decaying of the trees; after a period of six years or more, the locality may become healthy again. (Boussingault.) The admixture of fresh water containing organic matter with sea-water in which sulphates are present, gives rise in hot climates to the evolution of miasmata; as proved by Georgini in Italy, and by Daniell (p. 191) on the west coast of Africa. The conversion of the alkaline sulphates into alkaline hydrosulphates by the organic matter appears to have some relation to the formation of the miasma. Hence, also, miasmata are produced after an overflowing of the land by sea-water; and, according to Savi, when a mineral spring containing salts of sulphuric acid overflows its borders. Elevated spots in the neighbourhood of unhealthy localities are frequently quite free from disease. A veil before the face is said to be a protection from miasmata. Hence the contagious matter would appear to be heavier than air, and to exist in it not in the form of vapour, but in fine flakes or particles. (Boussingault.)—Heusinger (*J. pr. Chem.* 8, 484) supposes, with great probability, that vegetable or animal organizations are contained in miasmata. [On Miasma or Malaria, see also Mac Culloch, *N. Quart. J. of Sc.* 2, 39; Hopkins, *Phil. Mag. J.* 14, 104; Savi, *Ann. Chim. Phys.* 78, 344.]

NITROGEN AND HYDROGEN.

A. AMIDOGEN. NH^2=Ad.

Not known in the separate state, but only in combination with certain metals and organic compounds.

The *Metallic Amides* (*Amidmetalle, Amidides Metalliques*) are formed: 1. By heating potassium or sodium in ammoniacal gas, which they absorb with separation of $\frac{1}{3}$ of the hydrogen.

$$K + NH^3 = K,NH^2 + H.$$

—2. On mixing certain metallic chlorides and metallic salts with aqueous solution of ammonia. Thus:

$$2HgCl + 2NH^3 = HgAd, HgCl + NH^4Cl.$$

(See more particularly *Mercury*.)—The amidogen in these compounds takes the place of oxygen, chlorine, or a similar salt radical; many of the compounds also are known only in combination with metallic chlorides or metallic oxides. (See *Theories on Ammonia*, pp. 428—430.)

B. AMMONIA. NH^3.

Ammonium, Volatile alkali, flüchtiges alkali, flüchtiges Laugensalz, Ammoniaque, Ammoniacum;—In the gaseous form: *Ammoniacal gas, Alkaline air, alkalische Luft, urinose Luft, Gas ammoniaque, Gas ammonium.* Regarded by Kane as *Amide of hydrogen, Hydramide, Amidide d'hydrogène.* HAd.

Sources.—In the air, as carbonate of ammonia (p. 412).—In sea-water. (Marcet, Pfaff.) In various mineral waters combined with hydrochloric or other acids, as in the saline springs at Cheltenham and Gloucester (Murray, *Phil. Mag. Ann.* 6, 284); in the ferruginous waters of Passy and Chaudes Aigues (Chevallier); in the waters of Bourbonne-les-Bains, Fais-Billot, St. Mart, Ste. Marguerite, Jaude, and St. Allyre. (Bastien, Chevallier & Aubergier, *J. Chim. Med.* 10, 33.)—In river-water, *e. g.* in the water of the Seine. (Collard de Martigny.)—In peat-earth. (Collard.)—As sal-ammoniac, in the rock-salt of Hall in the Tyrol, and in the common salt of Rosenheim, Friedrichshall, Oeb, Kissingen, and Dürkheim. (A. Vogel, *J. pr. Chem.* 2, 290.) In the sal-ammoniac of volcanos.—The rust of iron contains ammonia. (Vauquelin, *Ann. Chim. Phys.* 24, 99.) Specular iron, bloodstone, magnetic iron ore, ilvaite, and also sesqui-oxide of iron formed during a recent conflagration, not only disengage ammonia when heated, but give it up even to hot water, which on subsequent evaporation with hydrochloric acid, leaves sal-ammoniac. (Chevallier, *Ann. Chim. Phys.* 34, 109; also *J. Chim. Med.* 3, 173; also *Kastn. Arch.* 10, 388.) Hydrated sesqui-oxide of iron also from Marmato, extracted from the middle of a vein of great thickness by a deep boring, contains ammonia. (Boussingault, *Ann. Chim. Phys.* 43, 334.) Most kinds of clay evolve ammonia when digested with solution of potash. (Bonis, *Ann. Chim. Phys.* 35, 333; also *J. Pharm.* 13, 282.)—The ammonia in sesqui-oxide of iron and in clay has probably been chiefly absorbed from the atmosphere, but partly also formed by the oxidation of the iron in contact with air and water. (*Vid. seq.*) Ammoniacal salts are also contained

in the juice of many plants (Pleischl, *Zeitschr. Phys. Math.* 2, 156), and in most animal fluids, especially in the urine.

Formation.—1. *From inorganic substances.*—*a.* On burning a mixture of oxygen, nitrogen, and excess of hydrogen, nitrate of ammonia is produced. (Theod. Saussure.)—Water containing atmospheric air yields nitric acid at the positive pole of a voltaic battery and ammonia at the negative pole. (Sir H. Davy.)—A mixture of 1 volume of nitrogen gas with 3 volumes of hydrogen transmitted through a red-hot tube, does not yield ammonia. It likewise remains unchanged when confined by mercury having a stratum of dilute nitric acid on its surface, and sunk 540 metres or 295 fathoms deep in the sea, where it must sustain a pressure of 50 atmospheres. (Laroche, *Schw.* 1, 123 & 172.)—Neither does spongy platinum induce combination. (Kuhlmann.)

b. Hydrogen at the moment of being set free from another compound, *i. e.* in the *nascent state* (I. 37, 38), in contact with nitrogen gas, frequently produces ammonia. Moistened iron filings in contact with nitrogen gas or atmospheric air at ordinary temperatures, induce the formation of ammonia. (Austin, *Ann. Chim.* 2, 260; Chevallier, *Ann. Chim. Phys.* 34, 109; Berzelius, *Jahresbericht*, 8, 115.) Hall (*Ann. Chim. Phys.* 11, 42) did not succeed with the above experiment. In the preparation of *Æthiops martialis* also, in which the iron filings are covered with a deep stratum of water, ammonia is produced, because the water contains nitrogen gas in solution. (Kuhlmann.)—Moistened zinc filings contained in a bottle in which air is present, give rise to the formation of ammonia. (Collard de Martigny, *J. Chim. Med.* 3, 516.)—A wet mixture of iron filings and sulphur likewise produces ammonia when exposed to the air. (Austin.)—When liver of sulphur is fused with an equal weight of iron filings, and water dropt on the mass while still warm, ammonia is evolved. (Hollunder, *Kastn. Arch.* 12, 402.)—The hydrates of potassa, soda, baryta, or lime, disengage large quantities of ammonia, when heated with potassium, arsenic, zinc, tin, lead, or iron; with copper, very small quantities; and with gold and other noble metals, none. The ammonia is produced not only on heating the mixture in the air, but also on heating it in hydrogen gas. (Faraday.) The formation of the ammonia in an atmosphere of hydrogen is explained by Bischof (*Schw.* 45, 204) as arising from the difficulty of obtaining hydrogen gas perfectly free from atmospheric air and consequently of nitrogen gas. Moreover, as remarked by Reiset, when the oil of vitriol by which the hydrogen gas is to be evolved, contains nitric oxide or nitric acid, nitric oxide will be mixed with the hydrogen — a circumstance not previously taken into account. When iron filings are heated with a concentrated solution of potash merely to a temperature of 130°, either in the air or in hydrogen gas containing nitric oxide, hydrogen and ammonia are evolved; in pure hydrogen gas, however, this effect does not take place. (Reiset, *Compt. Rend.* 15, 162.)—When turmeric paper is laid on plates of zinc, lead, or iron, moistened with water, the paper becomes reddened in several places in the course of a quarter of an hour; on heating it, the colour disappears. If the wet plates are covered with white paper, and the latter after some time is introduced into a glass tube, ammonia is disengaged on the application of heat. (Becquerel, *Ann. Chim. Phys.* 52, 248.) —Smithy scales reduced to powder and ignited in a covered crucible, produce ammonia when moistened with water and kept in a vessel containing air. (Sprengel, *J. pr. Chem.* 1, 162.)—Hydrated protoxide of iron

precipitated from green vitriol, produces small quantities of ammonia in the air, till it is converted into hydrated sesqui-oxide. (Sarzeau, *J. Pharm.* 23, 218; also *J. pr. Chem.* 13, 178.)—When grey sulphide of antimony is boiled with carbonate of soda, in the preparation of mineral kermes, the liquid from which the kermes is deposited on cooling, evolves ammonia, especially if it has been repeatedly boiled with the undissolved sulphide of antimony. (Leroy, *J. Pharm.* 10, 554; also *Ann. Pharm.* 13, 140; also *J. pr. Chem.* 3, 108.) In this case, the hydrosulphuric acid is probably the source of the hydrogen. (See Herzog's experiment, p. 200.)

c. Nitrogen in the *nascent state* is capable of combining with hydrogen gas.—A mixture of 2 volumes of nitric oxide gas with 5 volumes of hydrogen passed over spongy platinum (p. 378) yields ammonia. (Hare.)—Nitric oxide gas passed together with hydrogen through a red-hot tube, yields ammonia only when the tube contains porous substances. Finely divided pumice-stone produces a very large quantity; still more is produced by sesqui-oxide of iron, which, when gently heated in the glass tube, quickly becomes ignited in the stream of gas; the oxides of zinc, tin, and copper act less energetically. The alternate reduction and oxidation of the metal doubtless contributes to the formation of the ammonia. (Reiset, *Compt. Rend.* 15, 162.)—A mixture of nitrous oxide and excess of hydrogen passed over spongy platinum or platinum black contained in a tube, undergoes no alteration at ordinary temperatures; but on heating the platinum, it yields a considerable quantity of ammonia.—In a mixture of nitric oxide or hyponitric acid vapour and hydrogen, cold spongy platinum becomes bright red-hot and frequently gives rise to dangerous explosions; the whole of the nitrogen is converted into ammonia. Platinum-black does not act till heated to redness, and does not become incandescent. Spongy platinum when cold does not affect hydrogen gas saturated with nitric acid vapour; but when heated, it becomes red-hot and converts all the nitrogen into ammonia. Platinum-black also does not act unless it is first heated, and even then does not become incandescent in the gaseous mixture. (Kuhlmann, *Ann. Pharm.* 29, 284.)

d. Both nitrogen and hydrogen in the *nascent state.*—Moist nitric oxide gas transmitted over red hot iron filings yields ammonia. (Milner, *Crell. Ann.* 1795, 1, 554.)—Nitric oxide gas in contact with moistened iron or tin filings, aqueous hydrosulphuric acid, or the aqueous solution of an alkaline hydrosulphate or hydrosulphite, is decomposed, with formation of ammonia. (Kirwan, Priestley, Austin, H. Davy.)—Hyponitric acid decomposes aqueous hydrosulphuric acid, with formation of a small quantity of ammonia. (Johnston, Millon.)—In the decomposition of nitric acid by tin, nitrate of ammonia is one of the products. (Priestley, *Scheme* 85.) The same thing occurs with zinc, cadmium, and iron, but not with potassium or sodium. (Kuhlmann, *Ann. Pharm.* 27, 37.) A mixture of iron filings and very dilute nitric acid left over night in a suitable vessel, was found to be covered with an efflorescence of carbonate of ammonia. (Fabbroni, *Scher. J.* 8, 323; also *Gilb.* 5, 359.)—Iron filings covered to a finger's depth with a mixture of 1 part of fuming nitric acid and 6 parts of water, evolves in the course of a few days a large quantity of ammonia; with 12 parts of water, a smaller quantity; and with 16 parts, none at all. (Bischof, *Schw.* 56, 125.)—Zinc filings covered with a solution of nitrate of copper, produce ammonia. Iron filings mixed with nitric acid or with nitrate of copper in a close vessel exhale am-

monia after some time. (Austin.)—When nitrate of silver in solution is precipitated at the boiling point by means of iron, the liquid is found to contain ammonia. (Wetzlar, *Schw.* 50, 130.)—Dilute sulphuric acid mixed in proper proportions with nitric acid, dissolves zinc, iron, or tin without any evolution of gas, but sulphate of ammonia is formed at the same time. (Mitscherlich; see also I., 420.)—Nitre when ignited with hydrate of potash, does not evolve ammonia; but on the addition of zinc a large quantity is evolved. (Faraday.)—A mixture of 1 part of nitre and 3 parts of hydrate of potash heated with 20 times its weight of iron filings, gives off a large quantity of ammonia, besides hydrogen and nitrogen gases. (Döbereiner, *Schw.* 47, 120.)—Zinc, immersed together with iron in a solution of potash containing nitre, yields ammonia; whereas, if the nitre is absent, nothing but hydrogen is disengaged by the iron. (Döbereiner, *J. pr. Chem.* 15, 318.)—Ammonia is likewise formed in the decompositions of phosphide, sulphide, iodide, and chloride of nitrogen by water.

2. *From Organic Matter.*—*a.* When hydrate of potash, soda, baryta, or lime, is heated with sugar, linen, oxalates, tartrates, or many other organic compounds free from nitrogen, in a vessel containing atmospheric air or hydrogen gas, ammonia is disengaged. (Faraday.) (With respect to the hydrogen, *vid.* Reiset's observation, p. 417).—1 gramme of sugar mixed with an excess of soda-lime (that is, a mixture of 2 parts of lime and 1 part of hydrate of soda, prepared by mixing slaked lime with a solution of caustic soda, evaporating to dryness and igniting,) and heated to redness in a tube containing air, evolves a quantity of ammonia containing 0·0127 grm. of nitrogen. If hydrogen gas is passed through the tube for six hours previously, a quantity of ammonia is obtained equivalent to 0·0048 grm. of nitrogen. It appears, therefore, that a portion of the atmospheric nitrogen adheres to the porous mixture so tenaciously that it cannot be removed by the current of hydrogen. The formation of ammonia appears to depend upon this circumstance—that the charcoal produced when the mixture is heated, absorbs nitrogen from the adhering atmospheric air and produces a metallic cyanide, which on continuing the heat, undergoes mutual decomposition with the remaining alkaline hydrate, and ammonia is one of the products of the decomposition. If nitrogen gas be passed over a mixture of soda-lime and sugar during ignition, the quantity of ammonia obtained is not much larger; the charcoal appearing only at the moment of its elimination to be capable of absorbing the nitrogen already condensed in the pores of the mixture. (Reiset, *Compt. Rend.* 15, 134.)

b. Paste prepared from starch free from nitrogen, evolves ammonia during its decomposition in the open air. (Collard de Martigny.)

c. A mixture of olefiant gas, vapour of alcohol or nitrous ether, and nitric oxide gas, transmitted over heated spongy platinum, yields hydrocyanate of ammonia, besides other products. (Kuhlmann.) When a solution of platinum in aqua regia, still containing free nitric acid, is supersaturated with potash, mixed with alcohol, and exposed to the sun's rays, it deposits platinum black, and at the same time becomes continually richer in free ammonia: no nitrogen is absorbed from the air in this case; consequently the nitric acid combined with the potash must be the source of the nitrogen. (Döbereiner, *Schw.* 63, 476.) Nitre heated with gum (Vauquelin), or with $\frac{4}{5}$ of its weight of cream of tartar, produces ammonia. (Pagenstecher, *N. Tr.* 3, 1, 470.)

d. Most organic compounds containing nitrogen yield ammonia when

decomposed in various ways: namely by dry or destructive distillation, by heating with hydrate of potash, by putrefaction, by the vinous fermentation, &c. Ammonia is very frequently produced from cyanogen and its compounds. In this place may also be cited the observations of Woodhouse, Sir H. Davy (*Gilb.* 35, 471; 37, 163), and Hollunder (*Kastn. Arch.* 12, 402), whence it appears that an ignited mixture of potash and wood charcoal (which contains a small quantity of nitrogen), or ignited crude tartar (since crude tartar contains a ferment rich in nitrogen), evolves ammonia when moistened with water. For, cyanide of potassium is produced during the ignition and is decomposed on the addition of water by the heat evolved and the excess of potash present. Davy, however, found that a larger quantity of ammonia is obtained when the ignited mixture of charcoal and hydrate of potash is suffered to cool in contact with the air—a fact which accords with the observations of Faraday and Reiset (p. 419.)

Preparation.—1. *In the gaseous state:* 1 part of sal-ammoniac is mixed with 2 parts of pounded lime, and the mixture gradually heated in an iron or glass retort. (*Sch.* 63): $CaO + NH^3, HCl = CaCl + HO + NH^3$. The gas is collected over mercury.

2. *In the liquid state:*—*a.* From ammonio-chloride of silver (I., 286.) Chloride of silver saturated with ammoniacal gas and heated in one arm of the tube, fuses, and disengages ammonia with effervescence; the ammonia condenses in the other arm which is kept cool with ice. As the chloride of silver cools, the ammonia is again absorbed, with disengagement of heat which raises the temperature to 38° (100·4° F.), while the opposite branch of the tube becomes extremely cold. (Faraday.) For expelling the ammonia from the chloride of silver a heat of 112°—119° (234°.... 246° F.) is necessary. If the arm containing the chloride of silver is suffered to cool, the ammonia in the other arm begins to boil and cools it to + 6° (42·8° F.); but if the chloride of silver arm is rapidly cooled to + 12° (53·6° F.), the ammonia boils with great violence and that portion of the tube becomes covered with ice. (Niemann, *Br. Arch.* 36, 180.) —*b.* Ammoniacal gas is first passed through a long tube containing hydrate of potash, and then into a vertical tube, sealed at bottom, and cooled by a mixture of chloride of calcium and ice to a temperature of — 40°. (Bunsen, *Pogg.* 46, 102.) This tube, if kept as cold as possible, may afterwards be sealed at top also; Guyton Morveau (*Scher. J.* 3, 57) likewise condensed the gas by a cold of — 52°.

3. *In the solid state:* By Faraday's method (*vid.* I., 287.)

Properties. In the solid state, colourless, translucent, crystalline, heavier than the liquid; melts at —75° (—113° F.)—In the liquid state, colourless, and very mobile; of specific gravity 0·76; more refractive than water or liquid hydrosulphuric acid. (Faraday.) Boils under a pressure of 0·7493 met. at — 33·7° (28·2° F.) (Bunsen.) It conducts the current of a voltaic battery imperfectly and with slight evolution of gas, probably arising only from the presence of a trace of water. (Kemp.) The gas is colourless. [For the tension, specific gravity, and refractive power of the gas, *vide* I., 261, 280 and 95.] It has a very pungent, exciting and enlivening odour; animals die when immersed in it; it is not corrosive; tastes highly alkaline; reddens turmeric, even perfectly dry turmeric paper, and turns violet juice green; these changes of colour disappear however on exposure to the air. The gas is feebly combustible;

burns in immediate contact with the flame of a candle, with a pale light; but the combustion does not go on. It does not support the combustion of other bodies.

	Calculation.		C. L. Berthollet.	Am. Berthollet.
N	14	82·35	80·7	81·13
3H	3	17·65	19·3	18·87
NH^3	17	100·00	100·0	100·00

	Vol.	Sp. gr.		Vol.	Sp. gr.
Nitrogen gas	1	0·9706	=	½	0·4853
Hydrogen gas	3	0·2080	=	1½	0·1040
Ammoniacal gas	2	1·1786	=	1	0·5893

(NH^3 = 88·52 + 3 . 6·24 = 107·24. Berzelius.)

Decompositions.—1. *a.* When a succession of electric sparks is transmitted through ammoniacal gas rendered as dry as possible, it doubles its volume and is resolved into a mixture of 3 volumes of hydrogen gas and 1 volume of nitrogen. 100 volumes of ammoniacal gas were found by W. Henry, in his earlier experiments, to yield from 180 to 199 volumes; in his later experiment, from 200 to 204 volumes; C. Berthollet obtained 194, and Am. Berthollet 204 volumes, of decomposed gas. This gaseous mixture, according to W. Henry's first experiments, contained in 100 volumes, 26·25 nitrogen and 73·75 hydrogen gas; according to his last, 25 nitrogen and 75 hydrogen; and according to Am. Berthollet 24·5 nitrogen to 75·5 hydrogen gas.—*b.* A red heat effects the same decomposition,—for instance, the transmission of ammoniacal gas through a narrow glass tube (Priestley) or a porcelain tube (Am. Berthollet) heated to redness. Ammoniacal gas is scarcely acted on in an ignited porcelain tube when clean and empty, but more readily when it contains fragments of porcelain; with still greater facility when it contains platinum, silver, or gold wire; more easily still when it contains copper wire, and most quickly and completely when iron wire is introduced. These metals, for the most part, do not undergo any observable alteration in weight; but copper and iron become brittle, while gold and platinum remain perfectly unchanged. The higher the temperature, the more easily is the decomposition effected. (Thénard. Vid. *Metallic Nitrides*, *Nitrate of Iron*, and *Nitrate of Copper*.)

2. *a.* A mixture of 2 volumes of ammoniacal gas with not less than 1, and not more than 6 volumes of oxygen gas, may be exploded by the electric spark. In this case, when the oxygen is in excess, the products are nitrogen gas, water, and nitrate of ammonia, in the form of a cloud; when the ammonia predominates, nitrogen gas, hydrogen gas, and water are produced, because the unconsumed ammoniacal gas is resolved, by the heat disengaged, into its gaseous elements. (W. Henry.) Ammoniacal gas passed in a small stream into oxygen gas, may be set on fire and burns with a small yellow flame. (Berzelius.)—Ammoniacal gas mixed with atmospheric air enlarges the flame of a burning body, without, however, causing the combustion to proceed further; in whatever proportions the mixture may be made, it cannot be exploded by the electric spark; but a continuous succession of sparks induces slow combustion. (W. Henry.)—Spongy platinum does not affect a mixture of ammoniacal gas and oxygen; but on the addition of detonating gas, the platinum becomes red-hot, and causes the ammonia to burn. (Döbereiner.)—At a temperature of 193°, spongy platinum acts on a mixture of equal mea-

sures of ammoniacal and oxygen gases, water being slowly formed, and the nitrogen with the excess of oxygen left in the free state. (W. Henry, *Ann. Phil.* 25, 424.)—Platinum-black immersed in ammoniacal gas loses its power of inducing combustion, but causes the ammonia to absorb oxygen from the air and thereby to be decomposed into water and nitrogen gas; but the action is feeble, and soon ceases. (Döbereiner, *Ann. Pharm.* 1, 29.)—*b.* A mixture of ammoniacal gas with hypochlorous acid gas explodes violently, with separation of a large quantity of chlorine. Ammoniacal gas in contact with a concentrated aqueous solution of hypochlorous acid emits heat and a yellow light, and evolves nitrogen and chlorine gases. Aqueous ammonia, gradually added to an aqueous solution of hypochlorous acid, the mixture being constantly kept cool, yields nitrogen gas and oily drops of chloride of nitrogen; if the solutions are rapidly mixed, or if they are highly concentrated, heat is evolved, and a violent disengagement of chlorine and nitrogen gases takes place. (Balard.)—*c.* Chloric oxide gas yields with ammoniacal gas at ordinary temperatures, nitrogen gas, sal-ammoniac, and chlorate of ammonia. (Stadion.)—*d.* A mixture of ammoniacal gas and nitrous oxide—in which the former does not amount to less than $\frac{1}{7}$ or more than $\frac{3}{4}$ of the whole—explodes by the electric spark, yielding, when the nitrous oxide gas is in excess, water, nitrogen, oxygen, and a small quantity of hyponitric acid, while a small quantity of nitrous oxide remains undecomposed; when the ammoniacal gas predominates, the products are water, nitrogen gas, and hydrogen gas, together with a small quantity of undecomposed ammonia. In either case the original volume is but slightly diminished. (W. Henry.)—1 volume of ammoniacal gas will explode with 2·17 volumes of nitrous oxide, but not with 2·386 volumes or any greater quantity; even when the latter is in excess, the whole of the ammonia is not burnt; a portion is resolved into hydrogen gas and nitrogen gas. (Bischof, *Schw.* 43, 257.)—*e.* Ammoniacal gas, mixed with the proper proportion of nitric oxide, likewise explodes by the electric spark, yielding similar products. (W. Henry.) At ordinary temperatures, a mixture of equal volumes of ammoniacal and nitric oxide gases condenses, in the course of a month, to one half its original volume, without, however, undergoing complete decomposition; nitrogen gas, and probably also nitrous oxide, are among the products. Aqueous ammonia in contact with nitric oxide gas likewise produces nitrous oxide. (Gay-Lussac.)—*f.* Ammoniacal gas is rapidly and violently decomposed at ordinary temperatures, both by liquid and by gaseous hyponitric acid, with evolution of nitric oxide and nitrogen gases. (Dulong.) Ammoniacal gas and hyponitric acid vapour, when mixed in as dry a state as possible, and completely freed from air, undergo mutual decomposition, evolving great heat, and yielding nitrogen gas, water, and nitrite of ammonia; but in consequence of the formation of water and the impossibility of completely excluding the air, traces of nitrous oxide gas and nitrate of ammonia are also obtained. (Soubeiran, *J. Pharm.* 13, 329.) Probably thus:

$$4NH^3 + 3NO^4 = NH^3, NO^5 + 9HO + 5N.$$

[For the decomposition of ammonia in combination with sulphuric, selenic, iodic, periodic, bromic, hypochloric, chloric, perchloric, nitrous and nitric acids, refer to the corresponding salts.]

—*g.* Ammoniacal gas is decomposed by many metallic oxides, frequently below a red-heat, the products being water, nitrogen gas, a greater or smaller quantity of reduced metal, and occasionally also hyponitric acid

(p. 388); with other metallic oxides it forms water and a nitride of the metal.

3.—*a*. With ignited charcoal, ammonia yields hydrocyanate of ammonia and nitrogen gas. (Clouet, Langlois, *Ann. Chim. Phys.* 76, 111; also *J. pr. Chem.* 23, 232.)

$$2NH^3 + 2C = NH^3, HC^2N + 2H.$$

—*b*. Transmitted with vapour of phosphorus through a red-hot tube, it yields phosphuretted hydrogen gas and nitrogen gas charged with vapour of phosphorus; similarly with vapour of sulphur, it forms hydrogen gas, nitrogen gas, and a crystallized mixture of hydrosulphate and hydrosulphite of ammonia. (Fourcroy.) (For its decomposition with bisulphide of carbon, *vid.* p. 205.)—*c*. Iodine decomposes ammonia at ordinary temperatures, but only in contact with water, yielding iodide of nitrogen and hydriodate of ammonia.

$$4NH^3 + 6I = 3(NH^3, HI) + NI^3.$$

—*d*. Bromine and ammoniacal gas produce hydrobromate of ammonia, heat being evolved, and nitrogen gas set free. (Balard.)

$$4NH^3 + 3Br = 3(NH^3, HBr) + N.$$

—*e*. In chlorine gas, ammoniacal gas burns at ordinary temperatures with a red and white flame, yielding nitrogen gas and hydrochlorate of ammonia. In atomic proportions:

$$4NH^3 + 3Cl = 3(NH^3, HCl) + N.$$

By volume: 8 volumes of ammoniacal gas and 3 volumes of chlorine gas yield sal-ammoniac and 1 volume of nitrogen, inasmuch as 2 volumes of ammoniacal gas give up their 3 volumes of hydrogen to the 3 volumes of chlorine, to form 6 volumes of hydrochloric acid gas, which condense with 6 volumes of ammoniacal gas and form sal-ammoniac—while from the 2 volumes of ammoniacal gas decomposed, 1 volume of nitrogen gas is set free. When chlorine gas is passed in successive bubbles into concentrated aqueous ammonia, each bubble produces a slight explosion and a flash of light visible in the dark. (Simon, *Scher. J.* 9, 588.) If the chlorine is made to act upon ammonia in combination with a strong acid and dissolved in water, decomposition takes place more slowly, and the nitrogen separated from the ammonia unites with a portion of the chlorine. (Vid. *Chloride of Nitrogen.*)—*f*. Chloride of sulphur, under certain circumstances, decomposes ammonia, great heat being evolved and a variety of products formed. (Vid. *Sulphide of nitrogen with excess of sulphur, Ammonio-chloride of sulphur,* and the *compound of Ammonio-chloride of sulphur, with Ammonio-sulphide of nitrogen.*)—Bi-chloride of selenium decomposes ammoniacal gas with the aid of heat. (H. Rose, *Pogg.* 52, 64.)

Combinations, a. Aqueous Ammonia.—Liquid Ammonia, or simply *Ammonia; Spirit of Hartshorn, Salmiakgeist, ätzender Salmiakgeist, Spiritus salis ammoniaci causticus s. cum calce vivâ paratus.*

Ammoniacal gas is absorbed by water with great rapidity and considerable disengagement of heat. Ice rapidly absorbs the gas, and at the same time liquefies, with reduction of temperature. According to Davy, water at + 10°, and under a pressure of 29·8 in. absorbs at most 670 times its volume of ammoniacal gas, or nearly half its own weight; the specific gravity of a solution of this strength is 0·875. According to Dalton, water at a lower temperature absorbs even more than half its

weight; its specific gravity then falls to 0·850. At 24° (75·2 F.) 100 parts of water absorb 8·41 parts, and at 55° (131° F,) 5·96 parts of ammoniacal gas. (Osann.) 6 measures of water become 10 measures when saturated with ammoniacal gas. (Thomson.) 1 measure of water, by absorbing 505 measures of ammoniacal gas, forms a liquid occupying 1·5 measures, and of specific gravity 0·900; this when mixed with an equal bulk of water, yields a liquid of specific gravity 0·9455; consequently expansion takes place. (Ure.)

Preparation. Into the glass flask *a* (*App.* 50)—or, in preparing it on the large scale, into a vessel of earthenware, copper, or cast iron, furnished with an air-tight cover—1 part of sal-ammoniac (or sulphate of ammonia freed by gentle roasting from empyreumatic oil), is introduced in lumps and covered with cold milk of lime, prepared by slaking from $\frac{3}{4}$ to 1 part of lime with 3 or 4 parts of water. The vessel is then connected, as in the preparation of hydrochloric acid (p. 322), by means of three bent tubes, (the middle one being a Welter's tube) with three Wonlfe's bottles, the first of which contains a very small quantity of water, the second a quantity equal in weight to the sal-ammoniac employed, and the third a smaller quantity. The first two bottles are surrounded with cold water and moistened paper; a gentle heat is then applied, and is slowly increased—so that the mass may not boil over—till from one-fourth to half the water in the vessel *a* has distilled over into the first bottle *b*. In the first bottle a weak solution of ammonia is obtained, frequently coloured yellow from empyreumatic oil contained in the sal-ammoniac; this may be added in the next operation to the sal-ammoniac and milk of lime in the vessel *a*. In the second bottle a pure and concentrated solution of ammonia is obtained; if required to be perfectly saturated, the quantity of water in this bottle should not exceed $\frac{2}{3}$ of the sal-ammoniac. The third bottle contains very weak but pure ammonia.

Distillation from a retort or an alembic into a receiver, yields a less pure preparation.

If less water is added to the lime, the residue consisting of chloride of calcium and lime adheres more firmly to the bottom of the vessel. This solidification of the mass is in a great measure obviated, according to Wiegleb (*Taschenb.* 1781, 149), by the addition of a small quantity of common salt. The sal-ammoniac may also be heated with finely divided burnt lime, or with hydrate of lime slaked to a dry powder with a third of its weight of water. Either the two substances are mixed in the state of powder—whereby, however, a large quantity of ammonia is lost before the mixture is introduced into the vessel, and a fused mass is obtained on heating, which as it cools causes the glass vessel to crack—or the sal-ammoniac is placed in large pieces at the bottom and the powdered lime above it; in the latter case the volatilized sal-ammoniac leaves an empty space, by which the vessel is preserved from injury. This method is so far preferable, that for a given amount of product, smaller vessels may be employed, and the operation may be conveniently carried on in cast iron retorts very slowly heated. But a portion of sal-ammoniac volatilizes, and not only contaminates the liquid in the first bottle, but may also stop up the first bent tube, and thereby cause a dangerous explosion. A larger quantity of empyreumatic oil also passes over with the ammonia. Lastly, the resulting chloride of calcium obstinately retains a portion of the ammonia, and consequently diminishes the product.

Impurities in aqueous Ammonia: Carbonate of Ammonia. Occur when the lime used in the preparation contains a large quantity of carbonic acid, or the solution is afterwards exposed to the air. Renders lime water turbid, at least on the application of heat.

Chloride of Ammonium; carried over mechanically or in the form of vapour, into the first bottle. The liquid supersaturated with nitric acid, gives a cloud with solution of silver; leaves sal-ammoniac on evaporation.

Lime and *Chloride of Calcium;* mechanically carried over into the first vessel. Left behind on evaporating the solution.

Copper and *Tin;* when the still heads, condensing tubes, or bent tubes are made of copper. The liquid is turned brown by sulphuretted hydrogen, after being saturated with hydrochloric acid. The oxides are left behind on evaporation.

Empyreumatic oil; from the sal-ammoniac. Imparts a yellow colour and characteristic odour.

Properties. Colourless, transparent liquid. Specific gravity between 1·000 and 0·850, depending upon the amount of ammonia present. When concentrated, it does not freeze till cooled to between −38° and −41° (−36° and −42° F.); it then forms brilliant flexible needles; at −49° (−60° F.), it solidifies to a grey gelatinous mass, almost destitute of odour. (Fourcroy & Vauquelin.) Smells like ammoniacal gas, and has a sharp, burning, urinous taste. Loses the greater part of the ammonia at a temperature below 100°. According to Thomson, the gas is entirely expelled, even at 55°. (see, however, Osann's statement, p. 424.) On dissolving hydrate of potash in aqueous ammonia, bubbles of ammoniacal gas are disengaged, which are again absorbed by the upper portion of the liquid. (Waller.)

Amount of real Ammonia in Aqueous Ammonia of different Densities.

According to Dalton (*N. Syst.* 2, 230).			According to Sir H. Davy (*Elements* 1, 241).		According to Ure (*Schw.* 32, 58).			
Sp. gr.	Amm. per c.	Boiling point.	Sp. gr.	Amm. per c.	Sp. gr.	Amm. per c.	Sp. gr.	Amm. per c.
0·85	35·3	−4°	0·8750	32·3*	0·8914	27·940	0·9363	15·900
0·86	32·6	+3·5	0·8857	29·25	0·8937	27·633	0·9410	14·575
0·87	29·9	10	0·9000	26	0·8967	27·038	0·9455	13·250
0·88	27·3	17	0·9054	25·37*	0·8983	26·751	0·9510	11·925
0·89	24·7	23	0·9166	22·07	0·9000	26·500	0·9564	10·600
0·90	22·2	30	0·9255	19·54	0·9045	25·175	0·9614	9·275
0·91	19·8	37	0·9326	17·52	0·9090	23·850	0·9662	7·950
0·92	17·4	44	0·9385	15·88	0·9133	22·525	0·9716	6·625
0·93	15·1	50	0·9435	14·53	0·9177	21·200	0·9768	5·500
0·94	12·8	57	0·9476	13·46	0·9227	19·875	0·9828	3·975
0·95	10·5	63	0·9513	12·40	0·9275	18·550	0·9887	2·650
0·96	8·3	70	0·9545	11·56	0·9320	17·225	0·9945	1·325
0·97	6·2	79	0·9573	10·82				
0·98	4·1	87	0·9597	10·17				
0·99	2·0	92	0·9616	9·6				
			0·9632	9·5*				

In Davy's tables the three numbers marked with asterisks were determined by experiment, the rest by calculation. (Richter's tables, *Stöchiometrie,* 3, 233.)

Ammonia likewise combines:—*b*. With Phosphoric Oxide.—*c*. With Bisulphide of Carbon.—*d*. With Sulphide of Phosphorus.—*e*. With Iodine? —*f*. With Phosgene.—*g*. With Chloride of Boron.—*h*. With Chloride of Phosphorus.—*i*. With Chloride of Sulphur.—*k*. With Carbonate of Chloride of Sulphur.—*l*. With Fluoride of Boron.

m. With acids with which it forms the *Ammoniacal Salts*. Ammonia is capable of uniting with the hydrogen acids without the intervention of water. These compounds may be regarded in three different ways: —1. According to the old view, they are compounds of hydrogen acids with ammonia: thus, sal-ammoniac is NH^3, HCl. — 2. According to Kane, they are compounds of hydrogen acids with hydramide: HAd, HCl. — 3. According to Berzelius, they are compounds of ammonium (a substance resembling the metals in many respects, and containing 1 atom of nitrogen and 4 atoms of hydrogen,) with different salt-radicals. According to this view, sal-ammoniac is NH^4Cl, corresponding to KCl, NaCl, &c., the crystalline form of which it also possesses. When ammonia is added to a solution of chloride of glucinum, the latter theory supposes that the precipitation of the metallic oxide is accompanied by decomposition of water.

$$GCl + HO + NH^3 = NH^4Cl + GO.$$

With the oxygen acids, however, ammonia combines, for the most part, only in presence of water, 1 atom of which the salt obstinately retains, so that it cannot be expelled by heat without decomposition of the salt itself. This characteristic behaviour is explained by Berzelius in the following manner: The ammonium, NH^4, is converted by uniting with 1 atom of oxygen into oxide of ammonium, NH^4O, which like potass and other salifiable bases is capable of combining with oxygen acids. According to this view, sulphate of ammonia is not $NH^3, SO^3 + HO$ but NH^4O, SO^3. Kane regards ammonia, HAd, as a salifiable base isomorphous with HO, MgO, MnO, ZnO, FeO, CoO, NiO, CuO, in short with the bases of Graham's *Magnesia group*. In many instances, two of these bases—1 atom of each—are found intimately combined with 1 atom of acid. Thus, according to Graham, on heating white vitriol, $ZnO, SO^3 + 7Aq$, to a temperature of 100°, there remains a compound of 1 atom of sulphuric acid with 1 atom of oxide of zinc and 1 atom of water $= ZnO, HO, SO^3$, from which the water can only be expelled at a temperature approaching 238°. These salts, which contain 1 atom of acid to 1 atom of oxide and 1 atom of water, are the analogues of the ordinary ammoniacal oxygen-acid salts, the metallic oxide being replaced by hydramide; sulphate of ammonia for instance is: HAd, HO, SO^3.

Most of the ammoniacal salts may be formed by bringing ammonia or carbonate of ammonia directly in contact with acids.

Although the affinity of ammonia for acids is less than that of the other alkalis, it yet neutralizes them more completely. The ammoniacal salts have generally a pungent, saline, somewhat urinous taste.

All the ammoniacal hydracid salts, and likewise carbonate of ammonia, are volatilized by heat without decomposition; the other oxygen-acid salts when heated either evolve the ammonia undecomposed and leave the acid in its entire state (phosphoric acid), or the hydrogen of the ammonia combines wholly or in part with the oxygen of the acid—water being formed and nitrogen gas set free (as with sulphuric acid). Many ammoniacal oxygen salts, and even sal-ammoniac, when exposed to the

air at ordinary temperatures, and still more on the evaporation of their aqueous solutions, lose a portion of ammonia, so that the residue exhibits an acid reaction. Ammoniacal salts dissolved in water and treated with chlorine gas yield either hydrochloric acid and nitrogen, or, if the salt contains a powerful acid, hydrochloric acid and chloride of nitrogen. (Dulong.) An aqueous solution of hypochlorous acid yields with dry ammoniacal salts, water, chloride of nitrogen and nitrogen gas, while nitrogen and chlorine remain in solution. (Balard.) Fixed alkalis, oxide of lead, &c., rubbed up with ammoniacal salts, especially if a small quantity of water is present, disengage ammonia, which may be recognized by its odour, by the red colour which it imparts to turmeric paper, and by the cloud which a glass rod moistened with hydrochloric acid produces when held over the mixture. Magnesia expels only half the ammonia and forms a double salt. (*Sch.* 96.)

All ammoniacal salts dissolve in water and for the most part with facility. A solution, when not too dilute, gives a crystalline granular precipitate with concentrated sulphate of alumina (ammonia alum), with bichloride of platinum (chloride of platinum and ammonium), and, often after a long time only, with tartaric acid (bitartrate of ammonia). Only the most concentrated solutions of ammoniacal salts give a precipitate with perchloric acid, hydrofluosilicic acid, and carbazotic acid. Sal-ammoniac dissolved in so much water that 1 part of ammonia is contained in 100 parts of the liquid yields an abundant precipitate with solution of platinum; with 200 parts of water, a slight precipitate; with 400 parts, very slight indeed; and with 800 parts of water, a scanty precipitate after a lapse of 12 hours. (Lassaigne, *J. Chim. Med.* 8, 528.) Dilute alcohol heated with pounded ammoniacal salts and then set on fire, burns with a blue or violet flame.

The ammoniacal salts form numerous double salts with the salts of soda, magnesia, alumina, and the oxides of manganese, zinc, cobalt, nickel, copper, platinum, palladium, rhodium, iridium, and others.

The compounds of anhydrous oxygen acids with ammonia may be distinguished, according to H. Rose's nomenclature, as *Ammon-salts* (*Ammonsalze*). [Vide *Carbonate, Sulphite*, and *Sulphate of Ammon.*]

n. Aqueous ammonia forms solutions with numerous heavy metallic oxides, as with the sesqui-oxide of chromium, the oxides of tellurium, zinc, and cadmium, binoxide of tin, the protoxides of lead, iron, tin, cobalt and nickel, the dinoxide and protoxide of copper, and with oxide of silver; with the oxides of vanadium, uranium, antimony, mercury, silver, gold, platinum, and rhodium, ammonia likewise forms solid compounds, some of which are explosive.

o. With many *Anhydrous Oxygen-salts of Metallic Oxides*, which absorb ammonia abundantly and in atomic proportion, the combination being frequently attended with rise of temperature. The ammonia in these compounds replaces the water of crystallization; when heated, they evolve the ammonia wholly or in part, and are generally decomposed by water. (H. Rose, *Pogg.* 20, 147).

p. With many metallic iodides, bromides, and chlorides, which, sometimes by exposure to ammoniacal gas—the absorption being frequently attended with disengagement of heat—sometimes in the wet way,—combine, according to their nature, with $\frac{1}{2}$, 1, 2, or 3 atoms of ammonia, HAd, which in these compounds takes the place of water HO. Many of these compounds lose their ammonia even when exposed to the air; others, but not all, give it up when heated: in some cases, the application of

heat causes the sublimation of hydriodate, hydrobromate, or hydrochlorate of ammonia. Water decomposes the greater number of these compounds, either dissolving the haloid salt and separating the ammonia (chloride of calcium), or in other cases precipitating the metal in the state of oxide. Some of them however dissolve in water without being decomposed; and the solution frequently contains a portion of the ammonia in a condition similar to that in which it exists in anhydrous sulphate of ammon, so that solution of platinum precipitates only part of the ammonia from it. (*Vid.* Faraday, H. Rose, Persoz, Rammelsberg, in the memoirs referred to on page 370.)

q. With Fluoride of Silicium.—*r.* With Metallic Cyanides.—*s.* With many other organic compounds.

C. Ammonium. NH^4.

Kane's *Subamidide of Hydrogen.* $= H^2Ad$.

Not known in the separate state. Exists in the ammoniacal amalgam, combined with mercury; also according to Berzelius, in the ammoniacal salts, in combination either with the radical of the hydrogen acid, or as oxide of ammonium with the oxygen acid.

Theories relating to Ammonia.

1. *Old Theory:*—Ammonia, NH^3, is an alkali. It combines directly with hydrogen acids; thus, with hydrochloric acid it forms hydrochlorate of ammonia $= NH^3, HCl$. With oxygen acids, ammonia unites for the most part only when an atom of water is present, in which case the combination is perhaps rendered possible by the circumstance of the water containing hydrogen like ammonia, and oxygen like the ox-acid. According to this view, sulphate of ammonia is NH^3, HO, SO^3. The union of 1 atom more of hydrogen with the ammonia forms a compound, NH^4, which is known only in the form of the ammoniacal amalgam.

2. *Ammonium-theory of Berzelius.*—Formerly proposed by Ampère (*Ann. Chim. Phys.* 2, 6) but first consecutively followed out by Berzelius. Ammonia does not combine directly with hydrogen acids, but is converted, by uniting with the hydrogen of the acid, into ammonium, NH^4, which then unites with the radical of the acid. Thus, with hydrochloric acid ammonia yields chloride of ammonium $= NH^4Cl$. Ammonium, NH^4, is a compound metal, that is to say a compound substance having the chemical relations of a metal: when 1 atom of oxygen unites with it (or, what is the same thing, 1 atom of water, HO, with 1 atom of NH^3), a salifiable metallic oxide, the oxide of ammonium, is produced capable like oxide of potassium KO—with which it is isomorphous—of forming salts with oxygen acids. According to this view, sulphate of ammonia is more properly to be regarded as sulphate of oxide of ammonium $= NH^4O, SO^3$.

This theory presents the following advantages:—1. It explains the great similarity in physical and chemical characters, which the hydrochlorate of ammonia (considered as chloride of ammonium) bears to chloride of potassium and other metallic chlorides, that of iodide of ammonium to the metallic iodides, &c.—2. If the existence of the hydrogen-acid salts is denied (pp. 10—13) this view does away with the exception which

the compounds of ammonia with the hydrogen acids would otherwise create.—3. The theory sufficiently explains why the oxygen acids generally unite with ammonia only when water is present, the water having first to convert the ammonia into oxide of ammonium, which then forms the salifiable base.

On the other hand, the following considerations must be taken into account.—1. It is improbable that ammonia should be capable of separating the hydrogen from the chlorine in hydrochloric acid; at all events such separation supposes an extraordinary affinity of chlorine for ammonium.—2. If ammonia is not converted into a base—the oxide of ammonium—unless it takes up an atom of water, it is not very easy to see in what light ammonia is to be regarded, seeing that even in the anhydrous state it reddens turmeric, and has an alkaline taste and other alkaline properties.—3. Phosphuretted hydrogen PH^3 has a composition similar to that of ammonia NH^3, and forms both with hydriodic acid and hydrobromic acid, crystalline compounds similar to those of ammonia. Hence in accordance with the ammonium theory, the hydriodate of phosphuretted hydrogen, must be regarded as PH^4, I, and the existence of a hypothetical compound PH^4 allowed; or the compound must be viewed as PH^3, HI, and by this dissimilarity in the formula, the similarity in composition is lost sight of, whilst that of the physical and chemical characters is considerable.—4. It is remarkable that the oxide of ammonium, NH^4O, cannot be isolated.—5. Whether ammonium, if chemists could succeed in preparing it, would exhibit a metallic appearance, must for the present remain undecided.

3. Kane's *Amid-theory*. Amidogen, H^2N, is a feeble salt-radical; from its combination with 1 atom of hydrogen, results *Ammonia, Hydramide*, or *Amide of Hydrogen*, $=$ HAd. This compound is a base similar to HO and belonging to Graham's magnesian group of isomorphous elements: (CaO, MgO, MnO, ZnO, FeO, CoO, NiO, CuO.) It unites as such with the hydrogen acids, yielding for instance with hydrochloric acid: HAd, HCl. It forms similar compounds with metallic chlorides, &c., in which it replaces HO. It also combines with a few anhydrous oxygen acids, for instance, with sulphuric acid, forming HAd, SO^3, or according to the binary salt theory (pp. 14....16) H, SO^3Ad. Ammonium, according to this view, is a compound of 2 atoms of hydrogen with 1 atom of amidogen $=$ H^2Ad, or a *Subamidide of hydrogen*. The oxide of ammonium, NH^4O, of Berzelius, consists, according to Kane, of two salifiable bases, namely water and amide of hydrogen, $=$ HAd, HO. In the ordinary ox-acid ammoniacal salts, therefore, 1 atom of acid is combined with 1 atom of ammonia and 1 atom of water, that is to say, with 2 atoms of base. According to this view, sulphate of ammonia is HAd, HO, SO^3. Whilst HAd alone is isomorphous with the members of the magnesia group, HAd, HO is for the most part isomorphous with potash and soda. (I., 90.) This supposition is supported by the fact that CaO, HO in *Scolezite* replaces NaO in *Natrolite* (I. 89, 23). Whence it appears to follow that KO or NaO may be replaced by HAd, HO, or CaO, HO; in short, that 2 atoms of a base belonging to the magnesian group replace 1 atom of potash or soda in combination. The salts of zinc, nickel, copper, &c., cyrstallized from an aqueous solution, are also analogous to the ordinary ammoniacal salts in this respect, that they contain 1 atom of water in a state of intimate combination (p. 426).

Whatever may be the fate of these two theories, which no doubt have some truth in them, the following facts may be regarded as established:

NH^2 is a compound analogous to oxygen, chlorine, iodine, &c.; NH^3 is a salifiable base, probably isomorphous with water and with the bases of the magnesian group; NH^4 behaves like a metal; NH^3, HO or NH^4O is likewise a salifiable base isomorphous with potash and soda.

Nitrogen and Carbon.

[Cyanogen and the compounds connected with it will be discussed with the *Organic Compounds*.]

Carbonate of Ammonia.

a. Anhydrous Mono-carbonate of Ammon.—In whatever proportions ammoniacal gas and carbonic acid gas (both perfectly dry) are brought together, they condense slowly and with disengagement of heat, in the proportion of 1 volume of carbonic acid to 2 volumes of ammonia. (Gay-Lussac, J. Davy, H. Rose.)—1. A mixture of 1 volume of carbonic acid gas with 2 volumes of ammoniacal gas is passed through a number of glass tubes cooled down to a very low temperature. In these tubes the salt collects in the form of a sublimate; they are afterwards cut in pieces and the salt quickly extracted.—2. A mixture of anhydrous sulphate of ammon and carbonate of soda is sublimed in such a manner that no moisture can have access to it. (H. Rose.)

White mass which smells of ammonia (H. Rose); has a powerful alkaline action; volatilizes at a temperature just above 60°, and again condenses below 60°. (J. Davy.) (For the specific gravity of the vapour *vid.* I. 280.)

	Calculation.		H. Rose.
NH^3	17	43·59	44·69
CO^2	22	56·41	55·45
NH^3,CO^2	39	100·00	100·14

	Vol.	Sp. gr.
Ammoniacal gas	$\frac{2}{3}$	0·3929
Carbonic acid gas	$\frac{1}{3}$	2·5084
Vapour	1	·9013

Hence the two gases combine without condensation. (J. Davy; Bineau. *Ann. Chim. Phys.* 67, 240; H. Rose.) The salt may be repeatedly sublimed without change of composition. (H. Rose.)

Aqueous acids disengage carbonic acid from the salt, and fixed alkalis liberate ammonia. (H. Rose.) Chloride of calcium precipitates carbonate of lime from the aqueous solution, without causing any evolution of gas. (J. Davy.) Dry chlorine gas converts the anhydrous salt after some days into sal-ammoniac, carbonic acid, and nitrogen gas. The vapour of anhydrous sulphuric acid passed over it, expels carbonic acid and produces anhydrous sulphate of ammon. When heated in sulphurous acid gas, it yields on orange-coloured sublimate of anhydrous sulphite of ammon. It is decomposed in hydrochloric acid gas, on the application of heat, yielding carbonic acid and sal-ammoniac; heated in hydrosulphuric acid gas it forms hydrosulphate of ammonia. If not kept perfectly free from moisture, it appears to be converted into *b*. (H. Rose.) A solution of this salt in water behaves like a solution of the following salts mixed with a proportional quantity of ammonia. (Mitscherlich.)

b. Hydrated Mono-Carbonate of Ammonia.—1. Ordinary sesqui-carbonate of ammonia, or a mixture of sal-ammoniac and carbonate of soda, is gently heated in a retort, the neck of which is prolonged by a glass tube dipping into mercury; pure carbonic acid is first disengaged, and afterwards the compound *b* sublimes and is deposited at the end of the neck.

(J. Davy, H. Rose.) Towards the end of the process, other salts are sublimed.—2. The commercial salt is heated in alcohol or ether, and the sublimed salt *b* is freed by evaporation in vacuo over oil of vitriol from adhering alcohol or ether. (Hünefeld, *J. pr. Chem.* 7, 25; H. Rose.)—Crystalline; may be repeatedly sublimed without decomposition. Deliquesces in the air, dissolves readily in water, but cannot be recovered from the solution; because, even at ordinary temperatures in vacuo, ammonia is disengaged from it and an acid salt obtained. A very dilute solution does not precipitate chloride of calcium till after some time—a circumstance which is characteristic of the normal carbonate of ammonia. (H. Rose.)

	Calculation.		H. Rose.
$2NH^3$	34	39·08	39·27
$2CO^2$	44	50·58	50·09
HO	9	10·34	10·64
$2NH^3, HO, 2CO^2$	87	100·00	100·00

It must be regarded as $NH^3, CO^2 + NH^3, HO, CO^2$.

c. Five-fourths-Carbonate of Ammonia.—α. With 4 atoms of water.—Sublimes on slowly heating the ordinary sesqui-carbonate, and is deposited in crystal-line scales in the arch of the retort.

β. With 5 atoms of water.—1. Formed by subliming the variety of sesqui-carbonate of ammonia which contains 5 atoms of water.—2. By heating the salt *α* in a retort till it fuses to a clear liquid; carbonic acid is then evolved, and the salt *β* sublimed, while the fused residue solidifies on cooling, and forms salt *γ*.

γ. With 12 atoms of water. (H. Rose.)

	Calculation.		H. Rose.		Calculation.		H. Rose.		Calculation.		H. Rose.
$4NH^3$	68	31·78	31·13		68	30·49	30·53		68	23·78	22·70
$5CO^2$	110	51·40	52·92		110	49·33	48·56		110	38·46	38·31
4HO	36	16·82	15·95	5HO	45	20·18	20·91	12 HO	108	37·76	38·99
α.	214	100·00	100·00	*β.*	223	100·00	100·00	*γ.*	286	100·00	100·00

The salt *α* is considered by H. Rose as $3(NH^3, CO^2) + NH^4O, 2CO^2, 3HO$; it may also be regarded as $2(NH^3, HO, CO^2) + 2NH^3, 2HO, 3CO^2$.

d. Sesquicarbonate of Ammonia.—α. With 2 atoms of water. Sal Alkali volatile, Sal volatile salis ammoniaci; Commercial Carbonate of Ammonia;—as obtained by the dry distillation of bones, hartshorn, &c. and contaminated with empyreumatic animal oil: *Volatile salt of Hartshorn, flüchtiges Hirschhornsalz, Sal volatile Cornu Cervi.*—Obtained by heating a mixture of 1 part of sal-ammoniac (or sulphate of ammonia) and 2 parts of chalk, to incipient redness. On the small scale, a glass retort with glass receiver is employed; on the large scale, an earthenware or cast-iron retort with an earthenware or leaden receiver, which, when tolerably well filled by several distillations, is broken or cut in two.

$$3(CaO, CO^2) + 3(NH^3, HCl) = 3CaCl + (2NH^3, 2HO, 3CO^2) + NH^3 + HO.$$

The atom of NH^3 and the HO volatilize at the commencement, after which the salt *d* distils over in the form of a liquid into the receiver, where it rapidly solidifies. (*Vid.* O. Figuier, *J. Pharm.* 17, 237; also *N. Tr.* 24, 1, 252.)—The salt of hartshorn obtained by the destructive distillation of animal matter, may be also purified from the combustible oil which it contains, by subliming it once or twice with $1\frac{1}{2}$ times its weight of animal charcoal, in cast-iron vessels over which glass receivers are inverted. By repeated sublimation, however, the salt acquires a different compo-

sition, a mixture of the salts *b* and *c* being formed; on this account the commercial salt frequently contains excess of ammonia.

Impurities: Hyposulphite of Ammonia. This impurity occurs when sulphate of ammonia or sal-ammoniac containing sulphate of ammonia is employed in the preparation. The salt neutralized with acetic acid gives a white precipitate which rapidly turns black on the addition of nitrate of silver. (Pfaff, *Schw.* 55, 237.)—*Sulphate of Ammonia;* from the same sources. The salt neutralized with hydrochloric acid precipitates chloride of barium.—*Sal-ammoniac.* The salt dissolved in pure nitric acid, gives a white precipitate with solution of silver.—*Lead.* From the employment of leaden receivers. Imparts a grey colour to that portion of the salt which has been in contact with the receiver. The salt boiled with a slight excess of dilute nitric acid yields a solution which gives the reactions of lead.—*Lime* and *Chloride of Calcium;* from mechanical impurities; remain like other fixed substances, in the form of a permanent residue, when the salt is volatilized.

Transparent fibrous mass.

	Calculation.		Ure.	J. Davy.	H. Rose. 1	2	3	Kirwan.
$2NH^3$	34	28·81	30·5	27·39	28·66	30·7		24
$3CO^2$	66	55·93	54·5	54·58	50·55	53·4	56·23	52
$2HO$	18	15·26	15·0	18·03	20·79	15·9		24
d, a	118	100·00	100·0	100·00	100·00	100·0		100

The varieties 1 and 2 of the commercial salt examined by H. Rose, contained portions of the salt *c*, *β*. The salt may be regarded as $2NH^3$, $2HO,3CO^2$; or, according to H. Rose, as $NH^3,CO^2+NH^3,2CO^2,2HO$. The decomposition which the salt undergoes by exposure to the air, favours the latter view.

When the vapour of anhydrous sulphuric acid is passed over the salt, carbonic acid gas and ordinary sulphate of ammonia are obtained. In sulphurous acid gas, the salt remains unaltered at ordinary temperatures; on the application of heat, a yellow sublimate of anhydrous sulphite of ammon is first obtained, and then a white sublimate of hydrated sulphite of ammonia. When heated in hydrosulphuric acid gas, it is only partially converted into bi-hydrosulphate of ammonia. (H. Rose).—The salt when heated alone, evolves carbonic acid gas, the decomposition beginning at a temperature of 49°; afterwards the salt *b* is evolved together with a continually increasing quantity of sesquicarbonate of ammonia; and lastly, the same mixture with excess of water. (J. Davy.) After the salt *b*, the salt *c* sublimes; and in the retort there remains a clear liquid, which, on cooling, deposits crystals of sesquicarbonate of ammonia with 5 atoms of water, while monocarbonate of ammonia remains dissolved in the mother liquor. (H. Rose.)—The salt effloresces in the air, forming a friable mass of bicarbonate of ammonia, while anhydrous carbonate of ammon, *a*, sublimes; this takes place very rapidly if the salt is exposed in the state of powder. (H. Rose.) According to Mitscherlich, (*Lehrb.* 2, 100,) more than 1 atom of ammonia volatilizes for each atom of carbonic acid; hence a solution of chloride of barium, placed with the salt under an air-tight receiver, becomes ammoniacal in a short time. According to Dalton (*Ann. Phil,* 15, 137), pure ammonia is set free.—If the salt is treated with a smaller quantity of water than is required for perfect solution, the water dissolves out monocarbonate of ammonia, leaving bi-carbonate undissolved. (Dalton; Scanlan, *N*, *Bibl. univ.* 17, 182;—J. Davy;—H. Rose.)—Accordingly, if small quantities of water

are successively added to the salt, and poured off when saturated, the first solution shows the greatest specific gravity, the next, a lower specific gravity, and so on, in proportion as the more soluble monocarbonate decreases, and the less soluble bicarbonate increases in quantity in the solution. The first solution evaporated in vacuo leaves efflorescent crystals of monocarbonate of ammonia; the latter solutions contain bicarbonate only; the portions of bicarbonate which remain undissolved still retain the form of the salt *d*, originally employed. (Scanlan.)

On heating the complete solution obtained by using a larger quantity of water, carbonic acid gas is disengaged, with traces of ammonia, till monocarbonate of ammonia alone remains in the liquid. The solutions of the other salts which contain more than 1 atom of carbonic acid to 1 atom of ammonia, behave in a similar manner. (H. Rose.)—The salt when boiled with alcohol or ether, first evolves carbonic acid, and then yields a sublimate of the salt *b*. (Hünefeld, H. Rose.)—At ordinary temperatures, alcohol of specific gravity 0·829 removes nearly pure ammonia, together with a very small quantity of carbonic acid, and leaves bicarbonate of ammonia. More dilute alcohol also dissolves out a small quantity of monocarbonate of ammonia as well as free ammonia. (J. Davy.)

The solution of this salt in water is the *Spiritus salis ammoniaci aquosus*. In the old method of preparing it by distilling a mixture of sal-ammoniac with carbonate of potash and water, a liquid was obtained, which, if an excess of carbonate of potash were used, contained monocarbonate and also caustic ammonia, because the carbonate of potash was converted into bicarbonate.—When a sufficient quantity of water is employed to effect complete solution, 1 part of the salt at 13°, dissolves in 4 parts of water, at 16·7° in 3·3 parts at 32·2°; in 2·7 parts at 40·6° in 2·4 parts; and at 49° in 2 parts of water. From a hot saturated solution, the bicarbonate of ammonia crystallizes on cooling. (J. Davy.) Alcohol likewise precipitates crystallized bicarbonate from a saturated solution. (Fischer, *Schw.* 53, 123.) This precipitate was formerly called *Offa Helmontii*.

β. With 5 atoms of Water.—The salt *d*, *α*, is gently heated in a retort to the neck of which is adapted a glass tube dipping under mercury, till the residue fuses to a clear liquid. From the latter, after some weeks, the salt *d*, *β* crystallizes, leaving monocarbonate of ammonia dissolved in the mother-liquor.

Thin six-sided tables, which effloresce in the air and are converted into bicarbonate of ammonia. (H. Rose.)

	Calculation.		H. Rose.
$2NH^3$	34	23·45	23·56
$3CO^2$	66	45·52	45·55
$5HO$	45	31·03	30·89
d, *β*	145	100·00	100·00

e. Seven-fourths Carbonate of Ammonia.—Produced by distilling the bicarbonate containing 3 atoms of water.

	Calculation.		H. Rose.
$4NH^3$	68	20·60	19·41
$7CO^2$	154	46·67	47·70
$12HO$	108	32·73	32·89
e.	330	100·00	100·00

Probably: $NH^3, HO, CO^2 + 3(NH^3, HO, 2CO^2) + 8HO$?

f. Bicarbonate of Ammonia.—*α. With* 2 *atoms of Water.*—1. Obtained in one instance only in the crystalline form, by evaporating in vacuo a solution of the monocarbonate of ammonia.—2. Deposited in the form of a sparingly soluble powder, when a perfectly saturated solution of the ordinary sesquicarbonate is rapidly evaporated in vacuo over oil of vitriol; the powder must be quickly dried between folds of bibulous paper.—3. Remains as a crystalline mass, when an aqueous solution of the sesqui-carbonate is completely and slowly evaporated in vacuo, over potash, lime, or chloride of calcium.—4. Or when the + $\frac{2}{4}$-acid salt is evaporated over oil of vitriol. (H. Rose.)—5. Remains behind when the sesquicarbonate is kept in badly closed bottles. (J. Davy, H. Rose.)—6. Crystallizes from an aqueous solution of the sesquicarbonate, on saturating it with carbonic acid gas. (J. Davy.)—7. Precipitated from a solution of the sesquicarbonate by alcohol. (J. Davy.)—8. Sometimes formed in the preparation of carbonate of ammonia on the large scale. (Phillips, *Ann. Phil.* 17, 110.)

The salt obtained by the first method, has the same crystalline form as bicarbonate of potash, to which it corresponds in composition. (H. Rose.)

	Calculation.		Phillips. 8	J. Davy.	H. Rose. 1	2	3	5
NH^3	17	21·52	21·16	21·56	21·39	21·24	21·12	21·60
$2CO^2$	44	55·69	55·50	56·01	56·09	55·42	55·95	55·88
2HO	18	22·79	23·34	22·43	22·52	23·34	22·93	22·52
f, α	79	100·00	100·00	100·00	100·00	100·00	100·00	100·00

The numbers 8, 1, 2, 3, 5, refer to the different methods of preparing the salt.—Bicarbonate of ammonia may be regarded as NH^3, HO, CO^2 + HO, CO^2. (H. Rose.)

β. With $2\frac{1}{2}$ *atoms of Water.*—Sesquicarbonate of ammonia is digested in a strong bottle, with a sufficient quantity of boiling water to dissolve it, and the bottle immediately closed to prevent the escape of carbonic acid: When the solution thus obtained is allowed to cool gradually, it deposits the salt in crystals.

Large, transparent, colourless crystals, with smooth brilliant faces; belonging to the right prismatic system of crystallization. (*Fig.* 69) $u : u = 112° 9'$; $i : i = 136° 25'$; $y : y$ backwards $= 118° 33'$; $p : i = 158° 12{\cdot}5'$; $p : y = 149° 16{\cdot}5'$; $i : t = 111° 47{\cdot}5'$; $y : m = 120° 43{\cdot}5'$; $i : u = 101° 56'$; $y : u = 115° 5'$. Perfectly cleavable parallel to *u*. (G. Rose.) $u : u = 111° 48'$; $i : i = 135° 40'$; $y : y = 117° 40'$. (Miller, *Phil. Mag. Ann.* 6, 40; also *Pogg*, 23, 558.)

γ. With 3 *atoms of Water.*—Sublimes on heating the salt *c, β.* (H. Rose.)

	Calculation.		H. Rose.	Schrader.	Berthollet.
$2NH^3$	34	20·36	20·02	19	20
$4CO^2$	88	52·70	52·89	56	55
5HO	45	26·94	27·09	25	25
f, β	167	100·00	100·00	100	100

	Calculation.		H. Rose.
NH^3	17	19·32	18·12
$2CO^2$	44	50·00	50·67
3HO	27	30·68	31·21
f, γ	88	100·00	100·00

Schrader's and Berthollet's salt was obtained by saturating a solution of the sesquicarbonate with carbonic acid.

The salts *f, α, β,* and *γ* are inodorous, and have a slight but not alkaline taste, though they turn violet juice green. They volatilize more slowly than the monocarbonate, and without becoming opaque; according to J. Davy, they volatilize the more quickly in proportion to the quantity of moisture present in the atmosphere, because the water sets free a portion

of the carbonic acid. On this account, the vapour, as Schrader found, has an alkaline reaction. One part of the salt *f*, *a* dissolves at 12·8°, in about 6 parts of water; if a larger quantity of salt is added to the water, it evolves bubbles of carbonic acid gas, even at this temperature; at 38·7° the evolution of gas is rapid, and the liquid acquires an ammoniacal odour. Hence a solution of the sesquicarbonate of ammonia cannot be saturated with carbonic acid, at ordinary temperatures; and an aqueous solution of the bicarbonate, whether concentrated or dilute, becomes ammoniacal by keeping.—Bicarbonate of ammonia is not soluble in alcohol; but when exposed to the air under alcohol, it dissolves as monocarbonate with disengagement of carbonic acid. (J. Davy, *vid.* also Schrader, *A. Gehl.* 2, 582;—Berthollet, *N. Gehl.* 3, 555.)

g. Nine-fourths Carbonate of Ammonia.—A solution of sesquicarbonate of ammonia evaporated in vacuo over oil of vitriol, so slowly as not to enter into ebullition, deposits small crystals, which must be removed before they are converted by efflorescence into the salt *f*, *a*.—In consequence of the oil of vitriol absorbing the ammonia from the volatilizing carbonate, there remains an atmosphere of carbonic acid gas, which gradually combines with the salt left in solution.—The salt readily effloresces, losing carbonic acid and changing into the salt *f*, *a*.

	Calculation.		H. Rose.
$4NH^3$	68	19·10	19·12
$9CO^2$	198	55·62	55·83
$10HO$	90	25·28	25·05
g.	356	100·00	100·00

Nitrogen and Boron.

Borate of Ammonia.

a. Four-thirds Borate.—1. The salt *b* is dissolved in a covered vessel in hot and very strong ammonia; as the liquid cools, the salt *a* crystallizes out.—2. 100 parts of crystallized boracic acid, exposed for a considerable time to an atmosphere of ammoniacal gas, absorb 21 parts of ammonia. (Arfvedson).

	Calculation.		Arfvedson.
$3NH^3$	51·0	20·88	21·55
$4BO^3$	139·2	57·00	55·95
$6HO$	54·0	22·12	22·50
a.	244·2	100·00	100·00

b. Biborate.—Prepared by dissolving a moderately large quantity of boracic acid in hot aqueous ammonia, and slowly cooling; the act of solution is attended with rise of temperature.—The salt crystallizes in semi-transparent rhombic octohedrons, not so acute as those of sulphur, with truncated terminal summits, and frequently also with truncated edges. It has an alkaline taste and action. (Gmelin.)

	Calculation.		Gmelin.	Arfvedson.	Soubeiran.
NH^3	17·0	12·92	12·5	12·88	13·544
$2BO^3$	69·6	52·89	51·0	63·34	50·000
$5HO$	45·0	34·19	36·5	23·78	36·452
b.	131·6	100·00	100·0	100·00	99·996

Effloresces in the air and is converted, with loss of ammonia, into the

quadroborate. Soluble in about 12 parts of cold water. The solution evolves ammonia when heated.

c. *Quadroborate.*—Prepared by saturating a hot aqueous solution of ammonia with boracic acid, and slowly cooling. It forms colourless and transparent, irregular, six-sided prisms, belonging to the right prismatic system, with four, five, or six-sided summits. Appears tasteless at first, afterwards excites a burning, bitter taste; has an alkaline action on vegetable colours. (Gmelin.) Miller (*Pogg.* 23, 558,) describes borate of ammonia as crystallizing in square-based octohedrons, with the solid angles of the base perpendicularly truncated, and an inclination of the terminal edges = 105° 13′; he does not, however, state which of the three salts he examined.

	Calculation.		Gmelin.	Arfvedson.	Souberian.
NH^3	17·0	7·76	5·9	7·9	7·24
$4BO^3$	139·2	63·50	63·4	64·0	55·80
$7HO$	63·0	28·74	30·7	28·1	36·96
c.	219·2	100·00	100·0	100·0	100·00

Permanent in the air; when heated it swells up and fuses, leaving vitrefied boracic acid.—It dissolves in about 8 parts of cold water; this solution also gives off ammonia when boiled. (*Vid.* Lasonne, *Crell. Chem. J.* 5, 83;—Wenzel, *Lehre von der Verwandtschaft,* 355;—L. Gmelin, *Schw.* 15, 258;—Soubeiran, *J. Pharm.* 1134;—Arfvedson, *Pogg.* 2, 130.)

NITROGEN AND PHOSPHORUS.

A. PHOSPHIDE OF NITROGEN. N^2P.

Formed in the decomposition of ammonio-terchloride of phosphorus or ammonio-terbromide of phosphorus by heat.

Preparation.—1. Terchloride of phosphorus freed by repeated distillation from all excess of phosphorus, and surrounded by a freezing mixture, is slowly saturated with ammoniacal gas. The compound is then rapidly introduced—before it can absorb moisture from the air—into a wide tube of difficultly fusible glass, and the atmospheric air expelled by a current of dry carbonic acid gas. It is then heated in a strong charcoal fire for a considerable time, till no more traces of sal-ammoniac vapour are evolved, the current of carbonic acid gas being kept up throughout the process, and not arrested till the whole has become perfectly cold. (H. Rose.)—2. Vapour of terchloride of phosphorus is passed over sal-ammoniac, which is heated till it volatilizes. Hydrochloric acid and phosphorus escape, phosphide of nitrogen remains in bulky masses spotted with white, red, and brown.

$$2PCl^3 + 2(NH^3, HCl) = N^2P + 8HCl + P.$$

If pentachloride of phosphorus is used, a white phosphide of nitrogen is obtained, which however even after prolonged ignition in a current of carbonic acid gas, still retains between 1·5 and 3 per cent. of chlorine, besides hydrogen, and consequently evolves a small quantity of ammonia when ignited with copper. (Wöhler & Liebig.)

White bulky powder, which neither fuses nor volatilizes when exposed to a moderately strong red heat out of contact of air. If the ammonio-chloride of phosphorus contains moisture previous to

ignition, the resulting phosphide of nitrogen exhibits a reddish colour. (H. Rose.)

	Calculation.		H. Rose.	Wöhler & Liebig.
2N	28·0	47·14	47·32	49
P	31·4	52·86	52·68	51
N^2P	59·4	100·00	100·00	100

Decompositions.—1. Phosphide of nitrogen when heated in the air, evolves white fumes of phosphoric acid, and is slowly oxidized, without flame, producing phosphoric acid. (H. Rose.)—2. It is scarcely acted on by dilute nitric acid; strong nitric acid converts it very slowly into phosphoric acid. It dissolves in oil of vitriol, with disengagement of sulphurous acid; the solution contains phosphoric acid. (H. Rose.)—3. Explodes violently when heated with a nitrate. (H. Rose.) Also with chlorate of potash, chlorine gas being disengaged. (Wöhler & Liebig.) When fused with hydrate of potash it is readily decomposed, the decomposition being frequently attended with incandescence; when fused with hydrate of baryta, powerful incandescence invariably ensues; the results in both cases are nitrogen gas and hydrogen gas in about equal volumes, together with ammonia and phosphate of the fixed alkali. According to H. Rose, $2N^2P$ yields with 10HO from the alkaline hydrate, $2PO^5 + 3NH^3 + H + N$; but why the whole of the hydrogen is not employed in the formation of ammonia, according to the formula, $3N^2P + 15HO = 3PO^5 + 5NH^3 + N$, remains yet to be explained. An alkaline phosphate is also produced, with rapid disengagement of carbonic acid gas, when phosphide of nitrogen is ignited with carbonate of potash or soda. (H. Rose.)—4. When a mixture of phosphide of nitrogen and red oxide of mercury is heated, it fuses and is decomposed, with disengagement of light and heat—evolving vapour of mercury and leaving phosphate of mercury, which, on being further heated, leaves a residue of phosphoric acid. Again, when phosphide of nitrogen is heated with oxide of copper, flame and sparks are emitted and hyponitric acid formed. (Wöhler & Liebig.)—5. Dry sulphuretted hydrogen gas passed over ignited phosphide of nitrogen, volatilizes it completely in white clouds, which condense to a white or yellowish-white powder. This powder takes fire in the air at a summer-heat, and burns with a vivid white flame, leaving phosphoric acid. By nitric acid it is violently oxidized and dissolved, leaving only a small quantity of sulphur; the solution contains sulphuric acid and phosphoric acid. It also inflames in the vapour of hyponitric acid. When recently prepared, it is inodorous; but when exposed to the air for some time, it acquires the odour of hydrosulphuric acid. With water, it forms a milky solution which smells of hydrosulphuric acid, and deposits sulphur when kept out of contact of air; the supernatant liquid reddens litmus, and gives with chloride of barium, on the addition of ammonia, a copious precipitate of phosphate of baryta. With hydrate of potash it evolves ammonia; it dissolves completely in hot solution of potash, but not in solution of ammonia or in hydrochloric acid, which it renders milky. (H. Rose.) [Can this powder be $2NH^3, PS^6$ produced from $N^2P + 6HS$?]—6. Dry hydrogen gas transmitted over ignited phosphide of nitrogen, converts it into ammonia and phosphorus, which is deposited in yellow or brownish drops. Phosphide of nitrogen is not decomposed at a red heat by anhydrous chlorine, hydrochloric acid, carbonic acid, or ammoniacal gas; when moisture is present, hydrochloric acid gas gives rise to the formation of a

small quantity of ammonia. It is not decomposed when fused and distilled with sulphur. It is not altered in composition or dissolved, by dilute hydrochloric, sulphuric, or nitric acid, or even by boiling alkaline solutions. (H. Rose.)

B. Phosphamide.

Hydrate of Phosphide of Nitrogen.—Formed by saturating pentachloride of phosphorus with ammoniacal gas; extracting the greater part of the sal-ammoniac by washing with water; then removing the last portions of that substance, which adhere obstinately, by boiling first with caustic potash, and afterwards with nitric (or sulphuric acid), and finally washing with water.

White powder,—evolves ammonia when heated alone; when ignited with oxide of copper, it yields ammonia, white phosphide of copper, and a red fusible substance, which probably consists of phosphate of dinoxide of copper. (Wöhler & Liebig.)

¶ When heated alone, without access of air, it evolves ammonia, and leaves a new compound called *Biphosphamide* (p. 439). If it be moist when heated, it is resolved—completely, according to Gerhardt, incompletely, according to Gladstone—into ammonia and metaphosphoric acid. If the air has access to the substance while heat is applied to it, and the temperature is slowly raised to between 200° and 300° ammonia is evolved—the substance increases in weight (from oxidation)—and is converted into a dark-coloured mass, which is resolved by water into an insoluble portion consisting of biphosphamide, and an insoluble portion consisting mainly of phosphate of ammonia. Insoluble in water; but when boiled with that liquid it is very slowly decomposed, phosphoric acid and ammonia remaining in solution. The decomposition is accelerated by the presence of caustic potash, the ammonia being then evolved as gas. Sulphuric acid has no effect upon it in the cold, but decomposes it when heated, the solid matter entirely disappearing, and phosphoric acid and ammonia remaining in the solution: no sulphurous acid is evolved, but the liquid acquires a dark colour. To produce this effect, the sulphuric acid must be but very little diluted. When the substance is fused with caustic potash, ammonia is evolved and phosphate of potash remains. It resists the action of most oxidizing agents; is not affected by boiling in nitric acid, or a mixture of nitric and sulphuric acids; slowly oxidized by fusion with nitre; deflagrates when heated with chlorate of potash. Chlorine has no effect upon it, either in the cold or at any temperature short of that at which the substance itself is decomposed. Insoluble in alcohol or oil of turpentine. (Gladstone.)

According to Wöhler & Liebig.

	Calculation.		Exp.
2N	28	36·18	35·05
P	31·4	40·57	40·68
2HO	18	23·25	24·27
$N^2P, 2HO$	77·4	100·00	100·00

According to Gerhardt.

	Calculation.		Exp.
P	32	40·5	40·35
H^3	3	3·8	3·90
N^2	28	35·4	35·00
O^2	16	20·3	20·75
$PH^3N^2O^2$	79	100·0	100·00

According to Gladstone.

	Calculation.		Exp. *a.*	*b.*	*c.*
P	32	31·07	32·04	31·83	30·41
H^3	3	2·91	3·35	3·56	
N^2	28	27·19	27·29	27·69	
O^5	40	38·33	37·32	36·92	
$PH^3N^2O^5$	103	100·00	100·00	100·00	

Gladstone's results accord more nearly with the formula $P^2H^9N^4O^9$, which gives $32{\cdot}32\,P + 3{\cdot}03\,H + 28{\cdot}28\,N + 36{\cdot}36\,O$; but the formula $PH^3N^2O^5$ is rendered more probable by the mode of formation of the substance, inwhich it must be observed that oxidation plays an essential part:

$$PCl^5 + 7NH^3 + 2HO + 3O = 5(NH^4, Cl) + PH^3N^2O^5.$$

Gerhardt, on the other hand, maintains that chlorophosphamide, the substance formed by the action of ammonia on pentachloride of phosphorus, is composed of $PCl^3N^2H^4$, being formed in the manner represented by the equation:

$$PCl^5 + 2NH^3 = PCl^3N^2H^4 + 2HCl;$$

and that when this substance comes in contact with water, hydrochloric acid and phosphamide are produced:

$$PCl^3N^2H^4 + 2HO = 3HCl + PH^3N^2O^2.$$

This compound has not yet received an appropriate name; the term *Hydrate of phosphide of nitrogen*, originally applied to it by Wöhler & Liebig, is manifestly incorrect; and Gerhardt's name, *Phosphamide*, is liable to the objection that the nitrogen and hydrogen contained in the substance are not in the proportion to form amidogen.

¶ C. Biphosphamide.

Formed by the action of heat on dry phosphamide (p. 438), all the hydrogen and half the nitrogen in that substance being evolved in the form of ammonia, and the new substance, biphosphamide, remaining behind:

$$PH^3N^2O^2 \;=\; NH^3 + PNO^2 \quad \text{(Gerhardt)}$$
$$\text{or:}\quad PH^3N^2O^5 \;\; NH^3 + PNO^5 \quad \text{(Gladstone.)}$$

The phosphamide should be heated in a narrow tube open at one end, or better, in a gas containing no oxygen; because, if air has access to the heated substance, the action which takes place is altogether different. (Gladstone.)

Properties.—Grey powder, insoluble in all the ordinary menstrua, and showing no tendency to combine either with acids or with alkalis. Fuses at a full red heat, and on cooling, solidifies to a black vitreous mass: no combustion takes place; the weight remains unaltered. (Gladstone.)

According to Gerhardt.				According to Gladstone.			
Calculation.			Exp.	Calculation.			Exp.
P	32	51·6	50·6	P	32	37·21	38·82
N	14	22·6	22·4	N	14	16·28	16·33
2O*	16	25·8	27·0	5O	40	46·51	44·85
PNO^2	62	100·0	100·0	PNO^5	86	100·00	100·00

Decompositions.—When biphosphamide is moistened with water and heated, it is converted, but not completely, into phosphoric acid and ammonia. It is not affected by boiling with solution of potash; but when fused with solid hydrate of potash, it evolves ammonia and leaves phosphate of potash. Resists the oxidizing action of nitric acid, but deflagrates when fused with nitre. Unaffected by chlorine, both at ordinary temperatures, and when heated; iodine or sulphur heated with it, sublimes without

producing any change. Heated in a stream of hydrosulphuric acid gas prepared from sulphide of antimony, it assumes a dark, semi-fused, sticky appearance, and increases somewhat in weight. When it is heated in a current of hydrogen, ammonia is given off, and white fumes, consisting of phosphoric or phosphorous acid mixed with spontaneously inflammable phosphuretted hydrogen, pass along the tube; at the same time, a red substance—probably impure phosphoric oxide—sublimes in the tube, and water condenses. There is always a portion of the substance left which resists the action of the hydrogen.

According to Gerhardt, the residue obtained by heating chloro-phosphide of nitrogen does not consist of phosphide of nitrogen, as stated on page 436, but contains hydrogen, and is a mixture of biphosphamide with a compound of phosphorus, hydrogen, and nitrogen, whose composition is expressed by the formula PHN^2; this substance Gerhardt calls *Phospham.* According to Gladstone, however, this cannot be the case; for the substance in question (phosphide of nitrogen) is decomposed and rendered wholly volatile by hydrosulphuric acid; but biphosphamide is unaffected by that re-agent, and cannot therefore be present in the substance in question. Moreover, Gerhardt's own experiments give only 0·7 per cent. of hydrogen in the so-called *phospham*, whereas the formula PHN^2 requires 1·64 per cent.: hence it would be necessary to suppose the phospham to be contaminated with about its own weight of biphosphamide. (*Compare* Liebig & Wöhler, *Ann. Pharm.* 11, 139; Gerhardt, *N. Ann. Chim. Phys.* 18, 188; Gladstone, *Qu. J. of Chem. Soc.* 2, 121.) ¶

D. Compound of Phosphoric Oxide and Ammonia.

1000 parts of phosphoric oxide rapidly absorb between 48 and 49 parts of ammoniacal gas, but no more. The resulting compound is $NH^3, 5P^2O$. It is black, and loses part of its ammonia in a dry atmosphere, but retains the remaining portion so tenaciously that weak acids cannot separate it; sulphuric or hydrochloric acid, however, remove it rapidly with the aid of heat, or in 24 hours at ordinary temperatures, at the same time restoring the red colour of the phosphoric oxide. In an aqueous solution of ammonia, phosphoric oxide also turns black, but is rapidly converted into phosphuretted hydrogen gas and phosphate of ammonia. (Leverrier, *Ann. Chim. Phys.* 65, 266.)

With this compound also the following substance—discovered by Pelletier, and more accurately examined by Böckmann (*Vers. über das Verhatten des Phosphors in verschiedenen Gasarten;* Erlangen, 1800, *s.* 297), and by A. Vogel (*Gilb.* 45, 66; 48, 376), and considered to be phosphide of ammonia—appears to be identical. Phosphorus absorbs ammoniacal gas, especially under the influence of light, and is converted into a brownish-black powder, which, however, turns yellow after some days, unless moistened with solution of ammonia. The compound enters into slow combustion at a temperature just above 25°, but does not take fire till heated to 90°. In chlorine gas, it burns at ordinary temperatures with a much more brilliant yellowish-white flame than phosphorus itself. When heated, it turns red, but does not fuse below a red-heat, when ammonia and phosphuretted hydrogen gas are evolved. Hydrate of

potash disengages ammoniacal gas from it, and forms a soft brown substance, from which hydrochloric acid expels phosphuretted hydrogen gas. Hydrochloric acid separates but a small quantity of ammonia from the phosphide of ammonia, even at a boiling heat. (A. Vogel.)—Bineau (*Ann. Chim. Phys.* 67, 229) did not succeed in the attempt to form this compound; the phosphorus sublimed in the ammoniacal gas when exposed to the sun's rays, and became somewhat darker, but did not absorb ammonia. [Probably the presence of a trace of water is necessary, in order that phosphoric oxide may be formed under the influence of the solar light.]

E. Hypophosphite of Ammonia.

Deliquescent in the air, very soluble both in water and absolute alcohol. (Dulong.) Very much like the potash salt; when heated, it first evolves ammonia, and then leaves hydrated hypophosphorous acid, which is also decomposed on further exposure to heat. (H. Rose, *Pogg.* 12, 85.)

F. Phosphite of Ammonia.

An aqueous solution of phosphorous acid saturated with ammonia and evaporated to a syrupy consistence, yields large four-sided prisms with quadrilateral summits. When heated, the salt loses its ammonia, and leaves hydrated phosphorous acid, which at a higher temperature is resolved in the usual manner into phosphuretted hydrogen gas and phosphoric acid. The salt deliquesces rapidly in the air. (Fourcroy & Vauquelin—H. Rose, *Pogg.* 9, 28.)

G. Ordinary Phosphate of Ammonia.

a. Triphosphate? A concentrated solution of salt *b*, mixed with ammonia, solidifies to a magma, in consequence of the separation of salt *a*; in the air, however, the mixture gives off ammonia and is reconverted into salt *b*. (Berzelius.)

b. Diphosphate.—Formerly called *Neutral Phosphate.*—Occurs generally in combination with phosphate of soda and phosphate of magnesia, in the urine of carnivorous animals. To prepare it, carbonate of ammonia is added to aqueous phosphoric acid containing lime, till a further addition ceases to cause effervescence and precipitation of phosphate of lime; the solution is then filtered and evaporated, and the ammonia which volatilizes during the evaporation replaced, so that the liquid may have rather an alkaline than an acid reaction; it is then left in a cool place to crystallize. It forms large, colourless, transparent crystals, which belong to the oblique prismatic system. (*Fig.* 91, 43, 94, 95 & 96.) $i : axis = 113°\ 14'$; $i : u = 105°\ 22'$; $i : f = 109°\ 44'$; $u : u' = 84°\ 30'$; $i : a = 123°\ 20{\cdot}5'$; $f : axis = 137°\ 2'$; $f : u = 119°\ 28'$. (Mitscherlich.) $i : u = 105°\ 50'$; $i : f = 109°\ 32'$; $u : u' = 84°\ 15'$. (Brooke, *Ann. Phil.* 22, 285.) It has a cooling, saline, pungent taste, and alkaline reaction.

	Calculation.		Mitscherlich.
$2NH^3$	34·0	25·68	
cPO^5	71·4	53·93	54·426
$3HO$	27·0	20·39	
$2NH^4O, HO, cPO^5$	132·4	100·00	

The salt effloresces superficially in the air, and loses a portion of its ammonia, even at ordinary temperatures. When heated, it first undergoes the aqueous fusion—then dries up—and at a red-heat is converted, with slow and imperfect expulsion of ammonia, into hydrated phosphoric acid in a state of igneous fusion; according to Proust, the hydrated acid amounts to 0·62 of the salt. The salt dissolves in 4 parts of cold, and in a smaller quantity of hot water; the solution loses a portion of ammonia by the mere application of heat. The salt is insoluble in alcohol.

c. Monophosphate.—Formerly called the *Acid Phosphate.*—An aqueous solution of ammonia is treated with phosphoric acid, till the solution reddens litmus strongly and no longer precipitates chloride of barium. The salt belongs to the square prismatic system of crystallization. (*Fig.* 23 and 30.) $e : e' = 119° 46'$; $e : e^2 = 90° 25'$; $e : r = 135° 12·5'$. Not quite so soluble in water as *b.* (Mitscherlich, *Ann. Chim. Phys.* 19, 373.)

	Calculation.		Mitscherlich.
NH^3	17·0	14·73	
cPO^5	71·4	61·87	61·02
3HO	27·0	23·40	
$NH^4O, 2HO, cPO^5$	115·4	100·00	

Pyrophosphate of Ammonia.

Known only in the state of solution; as soon as the solution is evaporated, the acid takes up 1 atom of basic water, and yields crystals of E, *b.* (Graham, *Ann. Pharm.* 29, 19.)

Metaphosphate of Ammonia.

Likewise known only in the state of solution. When the solution is allowed to evaporate spontaneously, the salt is converted, on crystallizing, into E, *c.* (Graham.)

Nitrogen and Sulphur.

A. Sulphide of Nitrogen.

Preparation. The compound of protochloride of sulphur with 2 atoms of ammonia is prepared according to the second method, p. 482; (the compound obtained by the first method deposits free sulphur in addition to sulphide of nitrogen, on the addition of water); it is then decomposed with cold water, which principally dissolves sal-ammoniac and hyposulphite of ammonia, and separates sulphide of nitrogen. The latter is rapidly washed with cold water, till the liquid runs off colourless and free from chlorine. It is then washed twice with absolute alcohol to remove the water, pressed between folds of bibulous paper, and quickly dried in vacuo over oil of vitriol. Should it contain free sulphur, the latter must be removed by repeated boiling in ether. When sulphide of nitrogen is free from sulphur, it dissolves in hot water without leaving a residue. (Soubeiran.)

Properties. Light green powder. When heated to 100°, it becomes permanently yellow without alteration of weight; at ordinary temperatures

the same change takes place on exposure to ammoniacal gas or to the vapour of protochloride of sulphur. The sulphide of nitrogen prepared from the ammonio-chloride of sulphur, made according to the first method, is yellow from the commencement. Hence there are two isomeric states of this compound. It crystallizes from a solution in hot ether. When rubbed, it becomes highly electrical and tenacious; but if it has been turned yellow in an atmosphere of ammoniacal gas, it no longer exhibits these changes. It is inodorous except when heated, tasteless at first, but afterwards exhibits a transient pungent taste. When applied to tender parts of the skin, it produces itching. (Soubeiran.)

Calculation according to Soubeiran.

N	14	22·58
3S	48	77·42
NS^3	62	100·00

Decompositions—1. Resolved by heat into nitrogen gas and sulphur. A small quantity of undecomposed sulphide of nitrogen mixes with the nitrogen in the state of vapour, and may he recognized by its aromatic odour; it also forms a crystalline sublimate. The disengagement of nitrogen commences at 140° and slowly continues at this temperature; but when the compound is strongly heated, the evolution of nitrogen is attended with deflagration and explosion.—2. In cold water, sulphide of nitrogen disappears in a few days, but rapidly in hot water—being dissolved in the form of hyposulphite of ammonia with excess of acid.—($NS^3 + 3HO = NH^3 + 3SO$.) If the water contains an alkali in solution, the decomposition takes place more rapidly; in concentrated ammonia, the decomposition is attended with so much disengagement of heat, that ammoniacal gas free from nitrogen escapes with effervescence. In acidulated water, the decomposition takes place as in pure water, except that in the former case, sulphur is separated from the hyposulphurous acid.—3. Sulphide of nitrogen dissolves in absolute alcohol containing sulphide of sodium or soda in solution, and forms a dark hyacinth-red liquid; but the solution undergoes decomposition in a few seconds. (Soubeiran.)

Combinations. a. Sulphide of nitrogen dissolves in protochloride of sulphur, producing a dark reddish brown solution. If the solution is introduced into a tubulated retort surrounded with hot water, and carbonic acid gas passed through the tubulure, chloride of sulphur volatilizes, together with a small quantity of sulphide of nitrogen; yellow crystals of chloro-sulphide of nitrogen are sublimed (recognizable by the blue colour produced by ammonia); and in the retort there remains a red substance, which appears to contain an excess of chloride of sulphur.

b. Sulphide of nitrogen is very sparingly soluble in alcohol, but dissolves more readily in ether, from which it crystallizes on evaporation.

Sulphide of Nitrogen with a larger proportion of Sulphur? Gregory's *Sulphide of Nitrogen.*—Chloride of sulphur is slowly dropped into an aqueous solution of ammonia, in such quantity that the ammonia may remain in excess, and the mixture left to itself till the red compound first precipitated has become yellow. (Gregory, Soubeiran.) The precipitate obtained from chloride of sulphur saturated with sulphur, yields the maximum quantity of sulphide of nitrogen; the precipitate obtained with protochloride of sulphur, yields scarcely a trace. (Gregory.) In this manner,

a pale yellow, brittle mass is obtained which becomes red and soft at temperatures even below 100°. According to Gregory, it is to be regarded as a compound of his crystallized sulphide of nitrogen with excess of sulphur. According to Soubeiran, it evolves, when heated, a small quantity of nitrogen and ammoniacal gases in equal volumes, and leaves sulphur; with alcohol containing potash it yields an amethyst-red coloured solution, which rapidly becomes colourless in consequence of the formation of hyposulphite of potash. It gives up hyposulphite of ammonia to boiling water, the residue still possessing the property of reddening alcohol which holds potash in solution.

When the pale yellow substance is repeatedly boiled with large quantities of alcohol, it dissolves completely. The solution thus obtained, deposits crystals of sulphur on cooling, and by further evaporation and cooling more crystals are formed. The remaining mother-liquor yields Gregory's crystallized sulphide of nitrogen; the mother-liquor sometimes also contains a liquid lighter than water, of ethereal, pungent odour, and soluble in water and alcohol; it appears likewise to redden alcohol containing potash. (Gregory.)

Crystallized sulphide of nitrogen is colourless. When dried as completely as possible without the aid of heat, it is found to contain between 92 and 93 per cent. of sulphur and between 5·5 and 6·5 per cent. of nitrogen with a trace of hydrogen; hence its formula will be about NS^{12}. (Gregory.) When heated, it gives off rather more nitrogen and ammoniacal gas than the pale yellow substance. (Soubeiran.) With potash or lime it evolves ammonia only when heated, and forms sulphide of potassium or calcium. Its alcoholic solution assumes a splendid purple red colour on the addition of potash, ammonia, or baryta; a quantity amounting to no more than the $\frac{1}{100}$ part is sufficient for this purpose; the liquid, however, soon becomes colourless and deposits colourless crystals of hyposulphite of potash. An aqueous solusion of potash does not form a red coloured solution with sulphide of nitrogen. Sulphide of nitrogen is insoluble in water, but dissolves readily in alcohol. The solution at first tastes like wild fruit, then pungent, and lastly hepatic. (Gregory.)

B. *a*. Sulphite of Nitric Oxide. NO^2,SO^2.

Nitrosulphuric acid, Acide nitrosulphurique, Stickschwefelsäure.— Known only in combination with ammonia, potash, or soda.

The *Alkaline Nitrosulphates* are produced on bringing nitric oxide gas in contact with alkaline sulphites, or nitric oxide gas and sulphurous acid gas in contact with an alkali, at ordinary temperatures: an excess of alkali promotes the formation of the compound. When the nitric oxide gas predominates, the alkali absorbs 2 measures of nitric oxide gas for every measure of sulphurous acid, (consequently equal numbers of atoms, since sulphurous acid gas is monatomic, and nitric oxide gas di-atomic; *vid.* I., 66). An excess of nitric oxide gas remains unabsorbed; but when an excess of sulphurous acid gas is present, an alkaline sulphite is formed in addition to the nitrosulphate. (Pelouze.)

The compounds are colourless and crystalline. The composition of the ammoniacal salt is NH^4O,NO^2,SO^2; that of the potash salt, KO,NO^2,SO^2, Sir H. Davy, who first obtained these compounds, was of opinion that nitric oxide gives up 1 atom of oxygen to the sulphurous acid, and that a mixture of alkaline sulphate and a compound of nitrous oxide with the

alkali is obtained, which compound he called *Nitroxis.* Pelouze demonstrated, however, that the compounds crystallize entire. With respect to the manner in which the sulphur, nitrogen, and oxygen are combined in these compounds, the following views may be taken:—1. It may be NO^2, SO^2, or sulphite of nitric oxide.—2. It may be NO, SO^3, or sulphate of nitrous oxide.—3. Or it may be N, SO^4, a peculiar acid of nitrogen, corresponding to nitric acid, with 1 atom of oxygen replaced by 1 atom of sulphur. The last theory is that which is adopted by Pelouze.

The ammoniacal salt gradually evolves nitrous oxide gas at ordinary temperatures, and leaves sulphate of ammonia. The potash-salt is resolved, at a temperature of 130°, into nitric oxide gas and sulphite of potash. All acids, even carbonic acid, convert these compounds into nitrous oxide gas and a salt of sulphuric acid; many other substances act in the same way (vid. *Nitrosulphate of Ammonia* and *Potash.*)—An aqueous solution of these compounds does not decolorize sulphate of manganic oxide; hence they do not contain sulphurous acid. (Pelouze.)—This is not, however, conclusive, because the sulphate of manganic oxide is always very acid, and therefore immediately converts the nitrosulphuric acid into nitrous oxide and sulphuric acid. (Persoz.) The solution does not decolorize solution of indigo, and consequently contains no nitric acid. (Pelouze.)—This is likewise inconclusive; for the nitrates decolorize solution of indigo only on the addition of an acid. (Persoz.) The solution does not render baryta water turbid, but gives a precipitate with nitrate of baryta, which, after being washed with water containing potash, is found to be soluble in nitric acid, and is therefore not sulphate of baryta. (Pelouze.)

b. Sulphate of Nitric Oxide. $NO^2, 2SO^3$.

Formation.—1. Anhydrous sulphuric acid absorbs dry nitric oxide gas. (Aimé, H. Rose, Kuhlmann.)—2. When liquid sulphurous acid is shaken up with liquid hyponitric acid in a sealed glass tube, at ordinary temperatures, heat is evolved, and a greenish opaque mixture formed, which deposits sulphate of nitric oxide in the form of a yellowish white substance. The solid matter continues to increase, so that the mixture solidifies in the course of 24 hours to within $\frac{9}{10}$ of the whole, while the remaining $\frac{1}{10}$ forms a greenish liquid, which, on opening the tube, volatilizes in red vapours with great violence, and bursts the tube, unless it is surrounded with a freezing mixture. (Prevostaye.)

$$NO^4 + 2SO^2 = NO^2, 2SO^3.$$

The greenish explosive liquid, Prevostaye supposes to be nitrous acid; but, according to his observations, an explosion takes place on opening the tube, even after cooling the compound by means of a freezing mixture; whereas the boiling point of nitrous acid is certainly not far below —10°, and moreover nitrous acid is of a blue colour: hence the explosive liquid requires further investigation. According to Prevostaye, sulphurous acid and hyponitric acid do not act on each other in the gaseous form; and not even in the liquid state under the ordinary atmospheric pressure.—3. When anhydrous sulphuric acid is brought in contact with liquid sulphurous and hyponitric acids, this compound is immediately formed. (Prevostaye.) [Is there not in this case any free sulphuric acid left?]

Preparation.—1. Nitric oxide gas dried by means of chloride of calcium is passed over anhydrous sulphuric acid as long as it is absorbed.

The crust of the compound which forms prevents the sulphuric acid beneath from being saturated with gas. (H. Rose.)—2. Into one arm of a W-shaped glass tube liquid sulphurous acid is introduced, and into the other arm hyponitric acid, the two gases being in nearly equal volumes. Both ends are then sealed, and the two liquids, previously cooled by a powerful freezing mixture, are shaken together. After three days the tube is opened, after being first cooled in a freezing mixture to prevent explosion; and when the vapour of the greenish liquid is entirely expelled, it is again sealed and heated in an oil bath to 120° (248° F.). It is then reopened—upon which fresh red vapours escape, arising from portions of the greenish liquid enclosed in the solid compound; sealed once more; heated till the compound is completely fused, which takes place at about 230° (446° F.); and finally left to cool. (Prevostaye.)

Properties.—Crystallizes after fusion in regular rectangular prisms, often with two opposite lateral edges truncated; or in a white mass of silky needles, sp. gr. = 2·14. At 217° it begins to melt, and becomes perfectly fluid at 230°. When the compound has absorbed moisture from the air, the melting point is lower. The fused compound when near its boiling point is yellowish red, like hyponitric acid; at 230° it is yellow. It begins to solidify at 217°; at 190° the solid mass is transparent; below this temperature it appears opaque and greenish yellow, and is white only when perfectly cold. The compound boils nearly at the same temperature as mercury, and distils over without decomposition. It stains the skin dark red first, then yellow, and then slightly blackish. (Prevostaye.)—White, hard, does not fume in the air; when heated it melts, and may be sublimed unchanged. (H. Rose.)

Calculation, (according to H. Rose.)			H. Rose.	Or:			Prevostaye.
NO^2	30	27·27		N	14	12·73	11·79
$2SO^3$	80	72·73	71·64	2S	32	29·09	27·18
				8O	64	58·18	61·03
$NO^2, 2SO^3$	110	100·00			110	100·00	100·00

Prevostaye regards this compound (as in fact it was formerly regarded) as bisulphate of nitrous acid, or rather as $NO^4, SO^2 + SO^3$; according to this, it must contain 1N, 2S and 9O, with which its analysis agrees. H. Rose's view, however, is the more probable.

Decompositions.—1. Sulphate of nitric oxide dissolves rapidly in water, nitric oxide gas being evolved, and aqueous sulphuric acid remaining. When air is present, the nitric oxide gas evolved forms red vapours, and the liquid is found to contain a small quantity of nitric acid. Sulphate of nitric oxide deliquesces in the air, forming a permanent colourless liquid, which, however, gives off red vapours in contact with the moisture of the air. (H. Rose.) It emits hyponitric acid fumes in the air, but its decomposition takes place slowly, because the hydrated sulphuric acid produced protects the remaining portions from contact with the air. (H. Rose.) One gramme of the compound mixed with water evolves at most, only 50 cubic centimetres of nitric oxide, and the liquid still retains the odour of the gas. (Prevostaye.) With aqueous solutions of salts and alkalis, sulphate of nitric oxide behaves as with water; a solution of ferrous sulphate colours the smallest traces of the compound, brown. (H. Rose.)—2. Anhydrous baryta does not act on the compound at ordinary temperatures; when heated it becomes incandescent, and is converted into sulphate of baryta, with disengagement of red vapours.

(Prevostaye.)—3. Mercury also does not affect it at ordinary temperatures; when heated, it disengages a mixture of nitric oxide and sulphurous acid gas, and yields mercuric sulphate. (Prevostaye.)—4. It fuses in a current of ammoniacal gas, producing great rise of temperature, and forming a mass which is yellowish at first, but afterwards turns white; when completely saturated with ammonia the new compound behaves like ordinary sulphate of ammonia (NH^3, HO, SO^3) with a slight excess of sulphuric acid. Hence water must have been formed [and nitric oxide disengaged.] (H. Rose). Prevostaye, on passing ammoniacal gas through the fused compound, obtained acid sulphate of ammonia, with evolution of nitric oxide gas.—5. It converts alcohol into nitrous ether without the least disengagement of red fumes. (H. Rose.)

SULPHATE OF NITRIC OXIDE COMBINED WITH HYDRATED SULPHURIC ACID.—*a. Crystallized.*—*Formation* and *Preparation.*—1. By dissolving sulphate of nitric oxide in a small quantity of hot oil of vitriol. The greenish yellow solution solidifies, on cooling, to a translucent, nearly colourless mass. (Prevostaye.)—2. Oil of vitriol left in contact with nitric oxide gas for a period of two months, absorbs it gradually in such quantities, that white scaly crystals are produced. (O. Henry & Plisson, *Ann. Chim. Phys.* 46, 197.) According to Berzelius and Gay-Lussac, oil of vitriol does not absorb nitric oxide gas.—3. A mixture of oil of vitriol and hyponitric acid yields the crystallized compound, together with a liquid consisting of sulphuric and nitric acids.—$3NO^4$ is resolved into NO^2—which, in combination, with sulphuric acid and water, forms the crystals—and $2NO^5$, which, with the oil of vitriol, forms the mother liquid. Gay-Lussac obtained four-sided prisms by this process.—The formation of crystals proceeds more slowly in the latter case—in consequence of a larger quantity of nitric acid being produced—than when hydrated sulphurous acid is mixed with hyponitric acid. If the vessel in which the oil of vitriol and hyponitric acid are mixed is filled with nitric oxide gas, crystals are formed immediately. Anhydrous sulphuric acid mixes with hyponitric acid without any reaction; but, on the cautious addition of a small quantity of water, a portion of hyponitric acid volatilizes, and crystals are deposited; but however small the quantity of water added, a liquid compound invariably forms at the same time. (Gaultier de Claubry.)—Highly concentrated oil of vitriol absorbs from a mixture of oxygen and nitric oxide gases, 4 times its bulk of the former, and frequently more than 4 times its bulk of the latter, and at the same time becomes red and deposits crystals. (Bussy.)—When the vapour of hyponitric acid, evolved by heating a mixture of 1 part of starch and 10 parts of nitric acid of specific gravity 1·3, is passed through ordinary oil of vitriol, it is absorbed; and the oil of vitriol, which assumes a yellowish green colour, yields, on being shaken after some hours, a white crystalline mass and a mother-liquor containing oil of vitriol and nitric acid, besides a portion of the crystallized compound in solution. (A. Rose.)—The vapour of anhydrous sulphuric acid when brought in contact with fuming nitric acid, gives rise to the formation of crystals and of a liquid. (Döbereiner.)—4. Highly concentrated sulphuric acid decomposes nitric acid, at a somewhat elevated temperature, into oxygen gas and nitric oxide, which combines with the sulphuric acid.—Mono-hydrated nitric acid, HO, NO^5, kept cool by a freezing mixture, absorbs the vapour of anhydrous sulphuric acid in great abundance. When the liquid thus obtained is distilled, it first evolves oxygen gas and hyponitric acid vapour; after-

wards white needles sublime; and the residual liquid is a solution of sulphate of nitric oxide in oil of vitriol. (Kuhlmann.)—When oil of vitriol is mixed with concentrated nitric acid so slowly that no heat is evolved, the two acids appear to mix without alteration. The mixture when rapidly heated in a retort, gives off red vapours [and oxygen gas?] at first,—after which, sulphuric acid containing nitric acid distils over, and lastly pure sulphuric acid; the residue is a solution of sulphate of nitric oxide in oil of vitriol. (A. Rose.)—5. A mixture of sulphurous acid with hyponitric acid and water, yields—apparently with disengagement of gas—the crystalline compound of sulphate of nitric oxide with hydrated sulphuric acid. Sulphurous acid has no action on nitric oxide gas, nor on the hyponitric acid vapour produced on the admission of atmospheric air or oxygen gas, as long as water is not present; a small quantity of water causes the mixture to condense and form the crystalline compound. (H. Davy.) The crystals obtained in this manner are sometimes violet-coloured, probably because the nitric oxide gas when evolved from copper, carries a portion of copper with it.—Moist sulphurous acid gas produces the crystalline compound with liquid hyponitric acid; the hyponitric acid, however, gives off a small quantity of nitrogen gas in solitary bubbles, and a green mother-liquor containing hyponitric and nitric acids remains over the crystals. Liquid sulphurous acid mixes with hyponitric acid at $-20°$ without further action; but on the addition of a single drop of water, a violent disengagement of gas takes place, and crystals are formed, to which a small quantity of nitric acid adheres. (Gaultier de Claubry.) When a mixture of 1 atom of nitre and 2 atoms of oil of vitriol is distilled in a cast-iron vessel, a white crystalline mass is deposited in the receiver towards the end of the process; and this, on the addition of water, evolves nitric oxide gas—doubtless in consequence of the iron having reduced a portion of the sulphuric acid to sulphurous acid, which then acts on the red vapours. (Scanlan, *Kastn.-Arch.* 9, 405; *vid.* also Bernhardt, *Taschenb.* 1780, 41.)

The presence of oil of vitriol manifestly promotes the formation of the sulphate of nitric oxide.

In order to purify the crystals from the mother-liquor of sulphuric and nitric acids, Gaultier de Claubry washes them repeatedly with hyponitric acid; after which he introduces them into a tube, and passes dry air through, at a temperature between 20° and 30°, to expel the hyponitric acid.

Properties. Four-sided prisms (Gay-Lussac); or laminated, feathery, or granular crystallized masses; colourless, transparent or translucent. When gently heated, it fuses to an oily liquid; the larger the quantity of oil of vitriol present, the lower is the temperature required; the compound fused at 60° may be cooled down to 10° if kept at rest, and then on being shaken solidifies with disengagement of heat. (Prevostaye.) The heat evolved causes partial decomposition, according to Henry, Gaultier, and Thomson. (*vid. seq.*) This substance stains the hand yellow. (W. Henry.)

Approximate Calculation.			W. Henry. *a.*	Gaultier. *a.*	Thomson. *a.*
NO^2	30	17·86	10·32	18·89	12·08
$3SO^3$	120	71·43	68·00	65·59	83·39
$2HO$	18	10·71	21·68	15·52	4·53
$NO^2, 2SO^3 + 2HO, SO^3$	168	100·00	100·00	100·00	100·00

	W. Henry.	Gaultier.		Thomson.
	b.	*b.*		*b.*
NO^3	13·07	23·96	NO^5	21·75
SO^3	68·00	65·59	SO^2	66·70
HO	18·93	10·10	HO	11·55
	100·00	99·65		100·00

Henry and Gaultier are of opinion that the compound contains nitrous acid, sulphuric acid, and water; Thomson thinks that it contains nitric acid, sulphurous acid, and water; in accordance with which, they have given the analyses placed under *b;* the water was estimated by loss only. From the results obtained, the author has calculated the analyses under *a*, on the assumption that the compound contains nitric oxide. The analyses agree so little with each other, that no definite formula can be calculated. The want of uniformity is owing to the difficulty of obtaining the compound free from mechanically combined sulphuric acid, nitric acid, and water. According to Gaultier's analysis, an additional atom of water should be assigned to the compound.

Decompositions.—1. The crystals are decomposed by heat into nitric oxide gas and a solution of sulphate of nitric oxide in excess of oil of vitriol. At a temperature of 50° they begin to give off nitric oxide gas and hyponitric acid vapour; at 90° these products are evolved in greater abundance. The crystals soften at 100°, and fuse completely between 120° and 130°, disengaging at the same time a large quantity of hyponitric acid vapour; at 200°, the liquid evolves a small quantity of nitric acid; at 280° it is highly transparent, and of a yellowish-red colour, and evolves more nitric acid; at the boiling point of mercury, nearly colourless oil of vitriol distils over, and on the addition of water to this liquid, nitric oxide gas is evolved. (Gaultier.) The crystals remain undecomposed at 104·4°, and at 138° they give off nitric oxide gas; but even after the heat has been raised to 205°, a liquid remains which still evolves a large quantity of nitric oxide gas on the addition of water. (W. Henry.)—2. The crystals dissolve rapidly in water, with disengagement of heat and nitric oxide gas, yielding dilute sulphuric acid, which still retains a large portion of the nitric oxide in solution; on boiling the liquid, however, the nitric oxide is expelled. In contact with air, the nitric oxide gas evolved forms red vapours, which are partially absorbed by the aqueous solution and form nitric acid. The solution, when prepared in a close vessel and boiled for some time, is free from nitric oxide, and contains little or no nitric acid (the presence of the latter is recognised by the liquid giving a red colour with ferrous sulphate and oil of vitriol, p. 182, but not decolorizing hypermanganate of potash); the nitric acid when present, doubtless arises from portions of mother-liquor adhering to the crystals; but a solution formed in contact with air, contains nitric acid. (A. Rose.) 100 parts of the crystals dissolved in water in a retort evolve 12·08 parts of nitric oxide gas; the resulting solution is free from nitric acid. (Thomson.) On dissolving the crystals in water, the rise of temperature amounts to more than 33°; 100 parts of the crystals disengage in this manner 5·273 parts of nitric oxide gas, of which one half is set free immediately and the other half on boiling; the remaining liquid still contains, besides 9·31 parts of nitric acid, 68 parts of sulphuric acid [did the air have access to it?] (W. Henry.) When the crystals are exposed to the air, they first become pasty, and then deliquesce, giving off red vapours, and yielding an oily liquid which con-

tains sulphuric, nitric, and nitrous acids [nitric oxide]. (Gaultier.) The crystals when dissolved in water evolve red vapours even in an atmosphere of carbonic acid, hydrogen, or nitrogen gas, though in smaller quantity than in the air; the solution appears blue at first, then green, and lastly yellow. When laid on snow, the crystals melt, sinking into the snow like red-hot iron and imparting to it a dark blue colour: at the same time, the temperature falls as much perhaps as from $-1°$ to $-26·7°$, At $-26·7°$, no further action takes place. (Dana.)—3. When heated with magnesia, the crystals are decomposed, the whole mass becoming red-hot: with baryta, the action is still more violent, the mass being projected from the vessel. (Gaultier.) When rubbed up in a mortar with bicarbonate of potassa, the crystals first yield a dry mixture, and evolve nitric acid fumes [Nitric oxide gas?]; on continuing the rubbing, a pasty mass is produced, which in addition to sulphate and carbonate of potash, contains a minute quantity of nitrate. With carbonate of ammonia the crystals may be triturated without undergoing decomposition. (Thomson.)—4. When heated with mercury, the crystals yield sulphate of mercuric oxide with sulphurous acid, nitric oxide, and nitrogen. (Gaultier de Claubry.)

β. *Liquid Compound.*—1. Sulphate of nitric oxide dissolves abundantly in cold oil of vitriol. (H. Rose.) It does not dissolve in cold, and but slowly in hot oil of vitriol. (Prevostaye.)—2. The crystalline compound of sulphate of nitric oxide and hydrated sulphuric acid readily dissolves in oil of vitriol, (Gaultier); according to Dana, very slowly. —3. The liquid compound is also formed when an excess of oil of vitriol is present in any of the various methods of preparing the crystalline compound (pp. 447, 448). Döbereiner partially distils 3 parts of anhydrous sulphuric acid or fuming oil of vitriol with 1 part of fuming nitric acid; the residue in the retort is the liquid compound. A. Rose passes the vapour disengaged by heating 1 part of starch with 10 parts of nitric acid of specific gravity 1·3, into oil of vitriol.—4. Remains in the retort, on distilling the crystalline compound. Berzelius prepared it in this manner, and regarded it as sulphate of nitric acid.

Oily liquid, of specific gravity 1·887 (Döbereiner), between 1·94 and 1·96 (Berzelius); colourless at ordinary temperatures, bright yellow when hot; has a slight odour. (Döbereiner.) Colourless at ordinary temperatures, greenish yellow while hot (Prevostaye); colourless at ordinary temperatures, yellowish when hot; does not fume in the air. (H. Rose.)

When separated into two equal parts by distillation, the distillate contains less nitrous acid [nitric oxide] than the residue in the retort. When mixed with water, it evolves nitric oxide gas attended with great rise of temperature. When lime, magnesia, or hydrate of potash is mixed with the liquid, great heat is evolved, nitric oxide gas escapes with violent effervescence, forming hyponitric acid by contact with the air, and a sulphate of the base is produced. Heated with nitre, it froths up violently and evolves hyponitric acid fumes. Phosphorus inflames in it at a temperature of 62°, and emits red sparks. When distilled with sulphur, it yields nitric oxide, sulphurous acid, and a white sublimate. Sulphuretted hydrogen precipitates sulphur, first red, and afterwards yellow, with rapid disengagement of sulphurous acid gas; if water be then added, nitric oxide and nitrogen gases are evolved. Zinc, iron, copper, mercury, and silver are oxidized by the liquid, and colour it either purple, red (sulphide of iron gives the finest red), or violet-blue (the finest is obtained with copper). (Döbereiner.) During the solution of the metals,

nitric oxide gas is disengaged. (Berzelius.) Protochloride of iron is rendered dark brown and opaque by the liquid. The liquid compound is also decomposed by starch, sugar, alcohol, and ether. (Döbereiner.) When heated with sulphate of ammonia to 160°, it evolves pure nitrogen gas. (Pelouze.)

Sulphuric acid of specific gravity 1·6 dissolves the crystals with great difficulty, disengaging a small quantity of red vapour. At 15·5°, the pale-yellow solution evolves gas which is again absorbed at a lower temperature. (Dana.)

Upon the formation of sulphate of nitric oxide and its combination with oil of vitriol, is founded the *Preparation of English Oil of Vitriol.*

1. Sulphur is burned with about $\frac{1}{8}$ of its weight of nitre; whereby nitric oxide and sulphurous acid are evolved, and sulphate of potash remains behind—probably in the following manner:

$$KO,NO^5 + SO = KO,SO^3 + NO^2.$$

2. Nitric acid is placed in shallow dishes in the leaden chamber, into which the sulphurous acid gas is conveyed; or it is made to enter the chamber in the form of vapour, being evolved by heating a vessel containing a mixture of sulphuric acid and nitrate of potash or soda, in the flame of the burning sulphur. The nitric acid is decomposed by a portion of the sulphurous acid into sulphuric acid and nitric oxide gas:

$$NO^5 + 3SO^2 = NO^2 + 3SO^3.$$

3. A mixture of nitric oxide gas and hyponitric acid vapour, evolved by heating sugar, syrup, &c. with nitric acid, is passed into the leaden chamber. In all these cases, sulphurous acid gas, hyponitric acid vapour —formed from the nitric oxide gas and the oxygen of the air—and aqueous vapour, introduced for the purpose, mix together in the leaden chamber. By the mutual action of these substances, there is formed a crystalline compound of sulphate of nitric oxide with oil of vitriol, which falls in dense white clouds to the bottom of the leaden chamber, where it meets with water purposely placed there, and is resolved into sulphuric acid which is absorbed by the water and nitric oxide gas which escapes. The nitric oxide thus set free takes up a fresh portion of oxygen from the air, and again forms hyponitric acid vapour, which, as before, combines with sulphurous acid, and produces another portion of the crystalline compound, &c.

According to Kuhlmann, anhydrous sulphuric acid is capable also of combining with *nitrous* and with *hyponitric* acid.

On distilling a mixture of oil of vitriol and concentrated *nitric acid*, nitric acid (with oxygen gas?) is first evolved, and then pure oil of vitriol distils over; the residue contains sulphate of nitric oxide. (A. Rose.)

C. *a.* Mono-hydrosulphate of Ammonia.

Monosulphide of Ammonium. A mixture of 1 volume of hydrosulphuric acid gas with rather more than 2 volumes of ammoniacal gas, is passed into a tube cooled down to −18°. At ordinary temperatures, the two gases combine only in equal volumes, producing bi-hydrosulphate of ammonia. Berzelius recommends the sublimation of a mixture of sal-ammoniac and monosulphide of potassium, the latter not being in excess; according to the observation of Bineau, however (*vid. seq.*), the product will be mono-hydrosulphate or bi-hydrosulphate of ammonia, according as the receiver is cooled to −18° or not.

Colourless crystals, having a strong alkaline action, and at ordinary temperatures immediately evolving half their ammonia in the gaseous form. (Bineau, *Ann. Chim. Phys.* 70, 261.) An aqueous solution of the salt is obtained by dividing a quantity of aqueous ammonia into two equal parts, saturating one with hydrosulphuric acid gas, and then adding the other half. Colourless alkaline liquid, smelling of hydrosulphuric acid and ammonia; rapidly decomposed on exposure to the air (p. 225.)

Calculation.				Vol.
NH^3	17	50	Ammoniacal gas	2
HS	17	50	Hydrosulphuric acid gas	1
NH^3,HS	34	100		

b. Bi-hydrosulphate of Ammonia.

Double Sulphide of Hydrogen and Ammonium. Sulph-hydrate of Ammonia. At ordinary or at elevated temperatures, hydrosulphuric acid and ammoniacal gas invariably combine in equal volumes, in whatever proportions they may be mixed. (Bineau, *Ann. Chim. Phys.* 67, 230; 68, 435.) The two gases are made to pass in equal volumes into a vessel surrounded with ice, and previously filled with hydrogen or ammoniacal gas. The compound crystallizes in colourless needles and scales; it volatilizes and sublimes even at ordinary temperatures; has a penetrating odour of ammonia and of hydrosulphuric acid, and an alkaline action. Rapidly turns yellow in the air, from formation of pentasulphide of ammonium. (Thénard.) The salt yields a colourless solution with water. The same solution is obtained by saturating aqueous ammonia with washed hydrosulphuric acid gas, out of contact of air.

Calculation.				Vol.	Sp. gr.
NH^3	17	33·33	Ammoniacal gas	$\frac{1}{2}$	0·29465
2HS	34	66·67	Hydrosulphuric acid gas	$\frac{1}{2}$	0·58930
NH^3, 2HS	51	100 00	Vapour	1	0·88395

¶ *c.* Hypo-hydrosulphate of Ammonia.

Tetra-sulphide of Ammonium. Formed by passing ammoniacal gas and hydrosulphuric acid alternately through a solution of the pentasulphide *d.* It then separates as a crystalline mass. In its modes of decomposition it resembles the penta-sulphide. (*q. v.*)

Calculation.		
NH^3	17	20·73
HS	17	20·73
3S	48	58·54
NH^3,HS^4	82	100·00

(Fritzsche, *J. pr. Chem.* Bd. 33, abstr. *Ann. Pharm.* 52, 230.) ¶

d. Hydrosulphite of Ammonia.

Penta-sulphide of Ammonium. Aqueous solution of ammonia is saturated with hydrosulphuric acid gas, and sulphur in powder afterwards added, whilst ammoniacal gas is passed into the liquid. The excess of ammonia is then saturated by a current of hydrosulphuric acid gas; the

solution again treated with sulphur and ammoniacal gas, and lastly, with hydrosulphuric acid gas. After the final saturation, the solution, if kept cold, solidifies to a crystalline mass; it is then brought into the liquid state by heating to a temperature between 40° and 50°, and left to cool slowly in a stoppered bottle. (Fritzsche.) The crystalline compound is also obtained mixed with bi-hydrosulphate of ammonia, when a mixture of ammoniacal gas and vapour of sulphur is transmitted through a red-hot porcelain tube. (Thénard.)

Long, orange-yellow, oblique rhombic prisms. When heated, it gives off mono-hydrosulphate of ammonia, and is converted into hepta-sulphide of ammonium; similarly, when kept in a large vessel full of dry atmospheric air.

$$3(NH^4S^5) = 2(NH^4S^7) + NH^4S.$$

The crystals, if moist from adhering mother-liquid, acquire under these circumstances a ruby colour, increasing in size at first and becoming hollow inside. In the open air, the crystals gradually exhale hydrosulphate of ammonia, and are converted into a yellow mixture of crystallized sulphur and hyposulphite of ammonia. This decomposition takes place much more slowly in air dried by means of oil of vitriol. The compound dissolves in water, with separation of sulphur, which appears tenacious at first but afterwards becomes crystalline. The compound dissolves completely in alcohol, but the solution, even when kept in closed vessels, deposits crystals of sulphur under certain circumstances. (Fritzsche.) The solution obtained by saturating an aqueous solution of hydrosulphate of ammonia with sulphur at a gentle heat, is a brownish yellow, oily liquid, which does not fume in the air, and resembles hydrosulphate of ammonia, but has a less powerful smell.

	Calculation.		Fritzsche.
NH^3	17	17·35	17·120
HS	17	17·35	16·115
4S	64	65·30	64·700
NH^3,HS^5	98	100·00	97·935

The loss in Fritzsche's analysis arose from adhering mother-liquor.

e. Hypo-hydrosulphite of Ammonia.

Heptasulphide of Ammonium.—1. Formed by the spontaneous evaporation of *c*; the process succeeds best in a wide vessel containing dry air. —2. If the crystals of *c* are re-dissolved in the mother-liquor by the aid of heat, and the vessel containing the solution suffered to cool under a large receiver, which is ground to fit a glass plate, mono-hydrosulphate of ammonia escapes in bubbles, and *d* separates first in ruby-coloured crystals, then *c*, and lastly *d* again. The crystals may be preserved in bottles completely filled with them, and protected from heat and from the sun's rays; they change when exposed to the air, but not so quickly as *c*. When heated they evolve a lower sulphide of ammonium, which is deposited in yellow drops on the sides of the vessel, and leave sulphur: the yellow compound, on exposure to heat, yields a sublimate of very volatile crystals, probably consisting of bi-hydrosulphate of ammonia. The compound *d* assumes a brighter red colour when heated, and becomes surrounded with fused sulphur of a light yellow colour, into which the whole compound is gradually converted, with violent ebullition; but the still undecomposed portion of *d* neither fuses nor dissolves in the melted sulphur. A temperature not much higher than the melting-point of

sulphur is sufficient to decompose the salt. If the residual fused sulphur be allowed to cool in an atmosphere which contains the vapour of hydrosulphate of ammonia, it re-absorbs a large quantity, becomes orange-coloured, and remains liquid; on the application of heat it boils again. The residue of sulphur amounts to 75·32 per cent. (Fritzsche, *J. pr. Chem.* 24, 460.)

	Calculation.		Fritzsche.
NH^3	17	13·08	13·00
HS	17	13·08	12·92
6S	96	73·84	75·09
NH^3, HS^7	130	100·00	101·01

Volatile Liver of Sulphur, Spiritus sulphuratus Beguini, Liquor fumans Boylii, may be regarded as a mixture of hydrosulphate and hydrosulphite of ammonia dissolved in water. It is obtained by distilling a mixture of 1 part of sulphur with 2 parts of sal-ammoniac and 2 or 3 parts of lime. The liquid is obtained even when all the ingredients are anhydrous; so that the hydrogen required for the formation of the hydrosulphurous acid can only be derived from the hydrochloric acid, while chloride of calcium is produced, and the oxygen of the lime combines with a portion of sulphur, and forms sulphuric acid, which is retained by the undecomposed lime. (*Sch.* 108.)

$$4CaO + 3(NH^3, HCl) + 16S = 3CaCl + CaO, SO^3 + 3(NH^3, HS^5.)$$

But the quantity of sulphur which actually combines with 1 atom of hydrogen is less than 5 atoms. According to Gay-Lussac, free ammonia first passes over, and then bi-hydrosulphate of ammonia in crystals, which afterwards pass into the liquid state; the residue contains chloride of calcium, sulphate of lime, and sulphide of calcium; no nitrogen gas is disengaged. The liquid is also obtained when phosphate or sulphate of ammonia is used instead of sal-ammoniac; in this case, the hydrogen is derived from the water contained in the salt. (Gay-Lussac, *Ann. Chim. Phys.* 40, 302; also *Schw.* 55, 362; also *Pogg.* 15, 538; compare also E. *Crell. Chem. J.* 1, 56, who obtained one part of the distillate from 1 part of sal-ammoniac; also Vauquelin, *Ann. Chim. Phys.* 6, 42.) If slaked lime is employed, the product is more abundant but not so strongly concentrated. The distillate is dark yellow, and fumes in the air and in oxygen gas, but not in hydrogen or nitrogen gas. The first portions of the distillate, which contain excess of ammonia, have more especially the power of dissolving an additional quantity of sulphur, whereby an oily liquid is formed which no longer emits fumes, but deposits a portion of its sulphur on the addition of water.

f. Hyposulphite of Ammonia.

A solution of the salt yields by evaporation a soft mass consisting of small needles (Herschel); brilliant white scales very soluble in water (Zeise, *Schw.* 41, 183); when evaporated over oil of vitriol, it yields rhombic laminæ, which on exposure to heat give off water, ammonia, and a sublimate consisting of a mixture of sulphur with a large quantity of hyposulphite and sulphite, and a small quantity of sulphate of ammonia; the laminæ rapidly deliquesce in the open air. (Rammelsberg, *Pogg.* 56, 298.)

Calculation.			Rammelsberg.
$3NH^3$	51	22·08	
$3S^2O^2$	144	62·34	62·30
4HO	36	15·58	
$3(NH^4O, S^2O^2) + HO$	231	100·00	

g. Sulphamide. NH^2,SO^2.

The bisulphate of terchloride of sulphur mixed with the oil of olefiant gas (p. 342), forms with anhydrous ammoniacal gas, a cloud which condenses to a white powder. To prevent the powder from being partially fused and turned yellow by the heat thus disengaged, it must be artificially cooled from without. In order to insure complete saturation with ammonia, the mass is detached from the sides of the vessel and left in contact with ammoniacal gas for 24 hours. The excess of ammonia adhering to the mass is then removed by suspending it for several hours in vacuo over oil of vitriol.

The extremely deliquescent white powder thus obtained, may be regarded as a mixture of sal-ammoniac and sulphamide.

$$SO^2Cl + 2NH^3 = NH^4Cl + NH^2, SO^2.$$

Calculation.			Regnault.
2N	28·0	27·61	27·92
6H	6.0	5·92	6·16
Cl	35·4	34·91	34·78
SO^2	32·0	31·56	31·82
White Powder	101·4	100·00	100·68

The powder is very soluble in water and alcohol; the sal-ammoniac can only be partially separated from the solution by crystallization. From a solution of the powder in water, chloride of platinum precipitates but half the ammonia, namely the portion belonging to the sal-ammoniac. The solution does not precipitate chloride of barium at ordinary temperatures, even in the course of a year; a boiling heat promotes the precipitation, especially on the addition of a stronger acid; but after boiling the solution for 24 hours with chloride of barium and hydrochloric acid, but little more than half the sulphur present is separated in the form of sulphate of baryta; to obtain the whole of the sulphate of baryta, it is necessary to evaporate the mixture to dryness and redissolve in dilute hydrochloric acid.

If the chlorine of sal-ammoniac is precipitated from the solution by nitrate of silver, the filtrate still gives no precipitate with nitrate of baryta at ordinary temperatures. When the solution is boiled with potash for several hours, and the liquid afterwards saturated with hydrochloric acid, it still gives but a scanty precipitate with chloride of barium. A long time is therefore required for potash to convert sulphite of amidogen into sulphuric acid and ammonia. (Regnault, *Ann. Chim. Phys.* 69, 170; also *J. pr. Chem.* 18, 98.)

h. Anhydrous Bisulphite of Ammon.

Sulphit-Ammon. — Anhydrous sulphurous acid gas rapidly condenses with anhydrous ammoniacal gas to a light brown mass which is rendered colourless by water. (Döbereiner, *Schw.* 47, 120.) In whatever proportions the two gases are mixed, they always condense in equal

volumes. The dirty yellowish-red mass first obtained is converted, when kept for a long time at ordinary temperatures, into reddish-yellow needles collected together in stellated masses. (H. Rose.)

Calculation *a*.			Calculation *b*.		
NH^3	17	20·99	NH^3	17	20·99
$2SO^2$	64	79·01	SO	24	29·63
			SO^3	40	49·38
$NH^3, 2SO^2$	81	100·00	NH^3, SO, SO^3	81	100·00

According to calculation *a*, the salt is a compound of two atoms of sulphurous acid with one atom of ammonia; according to calculation *b*, of one atom of sulphuric acid with one atom of ammonia and one atom of SO; the SO would replace the atom of HO as it exists in ordinary sulphate of ammonia. H. Rose supposes with probability that the ammonia may be combined with an isomeric (or rather polymeric) sulphurous acid, S^2O^4 or SO, SO^3, that is to say, with an acid which may be regarded as a compound of hyposulphurous and sulphuric acid. Be this however as it may, the remarkable colour of the salt indicates a peculiar composition; and the singular changes which it undergoes, show the great tendency of the acid contained in the salt to separate into sulphuric and hyposulphurous acids, the latter of which is afterwards resolved into sulphurous acid and free sulphur. Millon (*Ann. Chim. Phys.* 69, 89) and Forchhammer (*Compt. Rend.* 4, 395), entertain the less probable opinion that a portion of the sulphur is combined either with nitrogen or with amidogen. Dumas regards the salt as NH^2, HO, SO, and calls it *Sulphimide*. But this formula supposes that the salt contains one atom of SO^2 to one atom of NH^3—a supposition which is in accordance with H. Rose's earlier experiments; whereas, according to his more recent researches, it appears to contain 2 atoms of SO^2 to 1 atom of NH^3.

The salt when exposed to the air becomes white and rapidly deliquesces; it dissolves readily in water. The solution, which is yellowish at first, soon becomes colourless and acquires a feeble acid reaction. When kept for a long time in close vessels, it deposits a small quantity of sulphur, probably in consequence of its acid being resolved into sulphuric and hyposulphurous acid. When a recently prepared solution is evaporated in vacuo over oil of vitriol at ordinary temperatures, a crystalline residue is obtained consisting of a mixture of ordinary sulphate and hyposulphite of ammonia [for this, however, the quantity of ammonia is too small]. Hydrate of potash disengages ammonia from the fresh solution, even at ordinary temperatures, and a larger quantity with the aid of heat; and if the liquid be then supersaturated with hydrochloric acid, sulphur is deposited, while sulphurous and sulphuric acid remain in solution. Hence the sulphurous acid must have combined directly with the potash in its proper form. A solution of the ammoniacal salt mixed with potash and evaporated in vacuo yields crystals of sulphate of potash, and a mother-liquor containing hyposulphite of potash. If a dilute solution of the salt is boiled with potash, till ammonia ceases to be evolved, sulphurous acid is obtained on the addition of hydrochloric acid, but no sulphur. The recently prepared solution, even if it has been previously boiled, yields sulphurous acid without separation of sulphur, on being mixed cold with hydrochloric acid, and the liquid turns red at a certain degree of concentration. But on boiling the fresh solution with hydrochloric acid, it evolves sulphurous acid and deposits sulphur, and the supernatant liquid is found to contain sulphuric acid. A solution kept for a long time out of contact of air yields sulphur, sulphurous acid, and sulphuric acid, even at ordinary tem-

peratures. A recently prepared dilute solution treated with oil of vitriol yields nothing but sulphurous acid; but a concentrated solution likewise gives a precipitate of sulphur. A recently prepared solution mixed with selenious acid at ordinary temperatures gives a red precipitate of selenium, just as common sulphite of ammonia does; but a solution kept for some weeks behaves like a hyposulphite, precipitating only a trace of selenium containing sulphur; but it precipitates a larger quantity on boiling, and a still larger quantity on the addition of hydrochloric acid. The freshly prepared solution yields with chloride of barium a precipitate of sulphate of baryta; and the filtrate, on the addition of hydrochloric acid, evolves sulphurous acid and deposits sulphur. In this case, the affinity of baryta for sulphuric acid appears to be the cause of the decomposition of $2SO^2$ into SO^3 and SO.—The recently prepared solution does not affect a solution of sulphate of copper at ordinary temperatures; on the application of heat, it precipitates sulphide of copper, like a hyposulphite. With corrosive sublimate, it gives a white precipitate which is converted into black sulphide of mercury when the ammoniacal salt is in excess. (just as with hyposulphite of ammonia; the ordinary sulphite does not precipitate corrosive sublimate.) With nitrate of silver also, the solution, whether new or old, behaves like a hyposulphite; when a small quantity only of silver-solution is used, the white precipitate re-disolves; with a larger quantity it is permanent, and then changes through yellow and brown to black; but the black sulphide of silver thus obtained also contains metallic silver, probably because a portion of the sulphurous acid remains unchanged and acts as such in the mixture. (H. Rose, *Pogg.* 33, 275; 42, 415.)

i. Sulphite of Ammonia.

α. Monosulphite or *Normal Sulphite.*—Sulphurous acid gas is passed through an aqueous solution of ammonia contained in a Woulfe's apparatus; combination takes place attended with rise of temperature. —Transparent and colourless six-sided prisms, with six-sided pyramids, of a fresh, pungent, and rather sulphurous taste.—The salt contains 29·07 per cent. of ammonia, 60·06 of sulphurous acid, and 10·87 of water. When heated, it decrepitates slightly, becomes soft without fusing, evolves a small quantity of ammonia and water, and then sublimes in the form of an *acid salt.*—When exposed to the air, it first becomes soft, and then hardens, in consequence of being converted into sulphate of ammonia. Nitric acid converts it, with disengagement of nitric oxide and sulphurous acid gases, into sulphate and nitrate of ammonia; chlorine converts it into sulphate and hydrochlorate of ammonia, with separation of sulphurous acid gas.—The salt dissolves in one part of water at a temperature of 12°, producing a considerable degree of cold; in hot water it is still more soluble. The solution evolves ammonia when boiled. (Fourcroy & Vauquelin, *Crell. Ann.* 1800, 2, 415.)

β. Bisulphite.—Prepared by saturating an aqueous solution of ammonia with sulphurous acid gas, or by subliming the salt *α.*—But the monosulphite and the bisulphite when heated on mercury to a temperature of 134°, do not give off gas, but are decomposed and blacken the mercury. (Bineau, *Ann. Chim. Phys.* 67, 241.)

k. Hyposulphate of Ammonia.

Hyposulphate of baryta is precipitated by sulphate of ammonia, and the filtrate left to evaporate at ordinary temperatures.—Indistinct, capillary crystals, having a cooling taste like that of Glauber's salts.—When heated, the salt first loses water and then sulphurous acid; and the residue, which does not fuse till then, is decomposed on further exposure to heat, in a similar manner to sulphate of ammonia.—The salt dissolves in 0·79 parts of water at 16°, with evident reduction of temperature; the solution may be boiled without undergoing decomposition. It is not soluble in absolute alcohol. (Heeren, *Pogg.* 7, 172.)

	Calculation.		Heeren.
NH^3	17	15·89	
S^2O^5	72	67·26	
2HO	18	16·82	18·44
$NH^4O,S^2O^5 + Aq.$	107	100·00	

l. Anhydrous Sulphate of Ammon.

a. Sulphate of Ammon.—1. *Neutral Sulphate.*—The *Sulfamide* of Dumas.—The Vapour of anhydrous sulphuric acid evolved by heating fuming oil of vitriol is passed into a wide-necked bottle surrounded with snow and constantly turned round, to ensure a uniform deposition of the acid. Ammoniacal gas, well dried by means of hydrate of potash, is then passed into the bottle, still surrounded with the freezing mixture: it is absorbed with great disengagement of heat. Only the surface of the acid is converted into neutral sulphate of ammon; the interior portions are so far protected by the crust of salt formed, that only an acid salt is produced; even when the bottle is kept full of ammoniacal gas for a year, a small quantity only of the neutral, and a large excess of the acid compound is the result. The lighter neutral salt at top is carefully scraped off; when dissolved in water, it should not redden litmus. (H. Rose.) The residue serves for the preparation of *Parasulphate of Ammon.* (*Vid. seq.*)

White, anhydrous, amorphous powder, having a bitter taste similar to that of ordinary sulphate of ammonia; an aqueous solution of the salt is neutral towards vegetable colours. If an excess of ammonia has been made to act on it, it has an alkaline reaction; when mixed with the acid salt, an acid reaction. It is permanent in the air. If it contains portions of the acid salt, it becomes moist in the air, or even deliquesces. (H. Rose.)

	Calculation.		H. Rose. 1.	2.
NH^3	17	29·83	29·29	
SO^3	40	70·17	70·75	70·04
NH^3,SO^3	57	100·00	100·04	

This compound is regarded by Kane as oil of vitriol (HO, SO^3) in which the compound of hydrogen with oxygen is replaced by a compound of hydrogen with amidogen = HAd, SO^3, or, according to the binary theory of salts = H, SO^3Ad;—SO^3Ad being a different salt-radical from *sulfan* (SO^4), and the precipitation of baryta, &c. being less readily effected by it. We may also, with Dumas, regard this compound as

hydrated sulphite of amidogen $= NH^2, HO, SO^2$; at all events, sulphate of ammon, and more especially parasulphate of ammon, exhibit in their reactions great similarity with Regnault's sulphamide. (H. Rose.)

When heated in the open air, it evolves sulphurous acid, ammonia, and sulphite of ammonia, and fuses to a clear liquid, which solidifies on cooling, and forms acid sulphate of ammonia. When it is heated in hydrogen gas, free ammonia and sulphite of ammonia pass over, the latter of which partially forms a yellowish sublimate, and the residue consists of acid sulphite and sulphate of ammonia.

The salt dissolves in about 9 parts of cold water. The solution does not change by long keeping. With potash, lime, or carbonate of potash, it gives off its ammonia at ordinary temperatures. (The anhydrous salt, when rubbed up in a mortar with carbonate of baryta or lime, does not yield any ammonia, unless the mixture is moistened with water.) An alcoholic solution of bichloride of platinum precipitates a solution of the salt immediately, but only throws down between 14·7 and 17·26 per cent. of ammonia, consequently little more than half. A solution of the salt gives a precipitate with sulphate of alumina, tartaric acid, racemic acid, or carbazotic acid, but only after a longer interval, and in much smaller quantity than an equally strong solution of ordinary sulphate of ammonia. The solution, when mixed with chloride of barium or nitrate of baryta, yields a portion only of its sulphuric acid in the form of sulphate of baryta; the precipitate is difficult to collect on a filter, because it runs through; moreover its quantity gradually increases, so that the liquid continually becomes turbid, even after repeated filtration. The precipitate obtained with chloride of barium at ordinary temperatures amounts in half an hour to 22·4, that obtained in one hour, to 23·5 per cent. of the sulphuric acid contained in the salt. On heating, the precipitate increases; but even after long boiling, with the addition of hydrochloric or nitric acid, the quantity of sulphuric acid precipitated amounts to no more than between 30 and 40 per cent., or about half the total quantity present. It is only by evaporating the solution to dryness with chloride of barium and strongly igniting the residue, that the whole of the sulphuric acid can be obtained in the form of insoluble sulphate of baryta. A solution of sulphate of ammon, even if previously boiled, does not render chloride of strontium turbid at ordinary temperatures; and even after the lapse of a week, it gives but a very scanty precipitate. On boiling, the mixture immediately becomes turbid; and after being evaporated to dryness and ignited till the whole of the sal-ammoniac is expelled, the residue of sulphate of strontia which remains undissolved after washing with water, contains the whole of the sulphuric acid formerly existing in the sulphate of ammon. Again, a mixture of the solution with chloride of calcium remains perfectly transparent even after a week, but becomes cloudy on boiling; and if it be evaporated to dryness and ignited, and the excess of chloride of calcium removed by alcohol, a quantity of sulphate of lime is left exactly corresponding to the quantity of sulphuric acid present. From a concentrated mixture of the two salts, alcohol precipitates unaltered sulphate of ammon even after the lapse of several weeks; sulphuric acid precipitates gypsum from the mixture. When the solution is digested with hydrate of lime till the whole of the ammonia is volatilized, a residue of ordinary gypsum is obtained. When solutions of sulphate of ammon and acetate of lead are mixed, the mixture at first remains clear, but gradually becomes turbid, and more rapidly on exposure to heat; the sulphuric acid, however, is but partially precipitated. (H. Rose.)

When a solution of sulphate of ammon is evaporated, it yields crystals of parasulphate of ammon and a mother-liquor containing the deliquescent salt. It is not mere solution that produces this change; evaporation seems to be necessary, inasmuch as a solution of sulphate of ammon exhibits different reactions from a solution of parasulphate of ammon.

Sulphate of ammon dissolves with difficulty in hot oil of vitriol, without evolving any odour of sulphurous acid and separates again on cooling. It is not soluble in alcohol, and does not undergo any change when digested with that liquid. (H. Rose.)

2. *Acid Sulphate of Ammon.* Produced simultaneously with the neutral sulphate in the form of a hard vitreous mass, which rapidly deliquesces in the air and dissolves in water with a hissing noise. (H. Rose.)

C. Parasulphate of Ammon. Crystallizes out on evaporating a solution of sulphate of ammon.—1. The solution is first evaporated at a very gentle heat, and then under a receiver over oil of vitriol; or the whole evaporation is conducted in vacuo over oil of vitriol, because the liquid gradually becomes acid when heated. The crystals of parasulphate of ammon are purified from the mother-liquor which contains the deliquescent salt, not by washing with water, but by pressure between folds of bibulous paper.—2. After the neutral sulphate of ammon has been removed from the bottle in which the anhydrous sulphuric acid was saturated with ammoniacal gas (p. 456), the remaining acid sulphate of ammon is left for a considerable time in contact with ammoniacal gas; the residual ammoniacal gas is then completely expelled by a current of dry air, and the open bottle left exposed for a long time to moist air; and lastly, the mass is very slowly dissolved in water. If any rise of temperature takes place, the excess of sulphuric acid converts the salt into ordinary sulphate of ammonia. The solution is freed from the excess of sulphuric acid by agitation with carbonate of baryta, filtered, and then evaporated as in the first method. If the ammoniacal gas is not entirely expelled by the current of air, a small quantity of ordinary sulphate of ammonia is produced, which cannot be separated by carbonate of baryta. (H. Rose.)

Colourless, transparent crystals belonging to the square prismatic system, but hemihedral (*Fig.* 40); of the 8 e-faces belonging to the primary form 4 are wanting; similarly with regard to the 8 a-faces of the first obtuse octohedron. $e : e = 91° \ 56'$; $e : a = 139° \ 28'$; $p : e = 113° \ 14'$; $p : a = 121° \ 15'$; the p-face is square, and rather uneven; the e and a faces are smooth and brilliant; the crystal has no plane of cleavage. (G. Rose.)

Parasulphate of ammon has the same composition as sulphate of ammon; it contains between 70 and 70·29 per cent. of sulphuric acid. (H. Rose.)

The crystals do not absorb moisture from the air unless a portion of the deliquescent salt adheres to them. When moistened with water and exposed to the air, they are converted, with separation of a small quantity of sulphuric acid, into the deliquescent salt. They are rather more soluble in water than sulphate of ammon; the solution is neutral and may be preserved unchanged in stoppered bottles, though the deliquescent salt appears to be gradually formed in the liquid. When evaporated in vacuo over oil of vitriol, it yields crystals of parasulphate of ammon mixed with a small quantity of the deliquescent salt; but if evaporated in the open air (which contains carbonic acid) the solution acquires the property of reddening litmus and is found to contain a larger amount of deliquescent salt. A solution of the salt in 9 parts of water

gives no precipitate with tartaric acid after several days; with racemic acid it yields, after some time, a much scantier precipitate than a solution of sulphate of ammon; it behaves like the latter solution with sulphate of alumina, bichloride of platinum, and carbazotic acid. The original solution does not affect the salts of baryta, strontia, lime, and lead, even after a long time. (It gives a precipitate, however, after it has become acid.) When boiled with chloride of barium, it gives a precipitate of sulphate of baryta, though the precipitate appears much more slowly than with sulphate of ammon; with chloride of barium and hydrochloric acid together, it yields a precipitate at ordinary temperatures, but not till after the lapse of 12 hours. When evaporated to dryness with excess of chloride of barium and ignited, the solution yields, after the excess of chloride of barium has been dissolved out with water, a quantity of sulphate of baryta which corresponds to only 67·47 per cent. of the sulphuric acid contained in the crystals, because a portion of the sulphuric acid volatilizes. (H. Rose.)

m. Deliquescent Sulphate of Ammon.

Remains in the mother-liquor after the crystallization of parasulphate of ammon. To free it as completely as possible from portions of parasulphate of ammon retained in solution, the aqueous solution of sulphate of ammon is suffered to evaporate to perfect dryness in vacuo over oil of vitriol; the residue exposed to the air till it undergoes deliquescence; the liquid poured off from the crystallized parasulphate of ammon; the solution evaporated till parasulphate of ammon crystallizes out; and, after the removal of these crystals, left to crystallize in vacuo. If the evaporation is conducted in the open air, the solution becomes slightly acid, and in that case must be neutralized by digestion with carbonate of baryta, and filtration, previous to the final evaporation in vacuo.

Ill-defined, needle-shaped crystals. When carefully prepared, the aqueous solution reddens litmus but very slightly.

	Calculation.		H. Rose.
$2NH^3$	34	27·65	
$2SO^3$	80	65·04	64.14
HO	9	7·31	
$NH^3, SO^3 + NH^4O, SO^3$	123	100·00	

This salt may be regarded as a compound of 1 atom of sulphate of ammon with 1 atom of ordinary sulphate of ammonia; the reactions of the solution, however, do not quite accord with this view of its constitution.

The aqueous solution behaves with sulphate of alumina, bichloride of platinum, tartaric acid, and racemic acid, like a solution of sulphate of ammon. It gives an immediate cloud with chloride of barium; but the precipitation of the sulphuric acid is as imperfect as in the case of sulphate of ammon,—only $\frac{1}{4}$ of the acid present being precipitated at ordinary temperatures in the course of 24 hours; the addition of hydrochloric acid causes about half to be thrown down. The solution precipitates a concentrated solution of chloride of strontium immediately, and a dilute solution after some time. It does not affect a solution of chloride of calcium. With acetate of lead it behaves in the same manner as a solution of sulphate of ammon. (H. Rose.)

n. SULPHATE OF AMMONIA.

a. MONOSULPHATE.—*Glauber's geheimer Salmiak, Sal-ammoniacum secretum Glauberi.* Occurs native as *Mascagnine.* Obtained by decomposing carbonate or hydrochlorate of ammonia with sulphuric acid. Colourless, transparent, crystals, which, in their form and the magnitude of their angles, correspond precisely with those of sulphate of potash. (Bernhardi, *N. Gehl.* 8, 413, and *N. Tr.* 9, 2, 25; Beudant, Mitscherlich, *Pogg.* 18, 168.) *Fig.* 76 & 77. $y:y$ below 121° 8′; $n:n$ = 111° 15′. (Mitscherlich.) Has a sharp, bitter taste.

	Calculation *a*.		Mitscherlich.	Ure.
NH^3		17	25·76	
SO^3		40	60·61	
HO		9	13·63	13·58 ... 13
NH^4O, SO^3		66	100·00	

	Calculation *b*.		Berzelius.	Kirwan.
NH^3	17	22·67	22·6	14·24
SO^3	40	53·33	53·1	54·66
2HO	18	24·00	24·3	31·10
NH^4O, SO^3, HO	75	100·00	100·0	100·00

According to Berzelius, the crystallized salt contains 2 atoms of water, 1 atom of which is expelled at a gentle heat; according to Mitscherlich (*Lehrb.* 2, 102), it contains but 1 atom of water. The latter statement—inasmuch as sulphate of ammonia and sulphate of potash form similar crystals—accords with the supposition that KO and NH^4O or NH^3HO, and therefore also NH^4O,SO^3 and KO,SO^3, are isomorphous compounds.

Sulphate of ammonia decrepitates when heated, melts at 140° (284° F.), and begins to decompose at 280° (536° F.), whereby the glass vessel is corroded. (Marchand, *Pogg.* 42, 556.) During decomposition, it evolves ammonia, then water and nitrogen gas, and disappears entirely, with sublimation of sulphite of ammonia and a small quantity of sulphate. When passed through a red-hot tube, it is resolved into water, sulphur, and nitrogen gas. (H. Davy, *Scheme* 68.) When heated with chlorate of potash, it is decomposed, becoming red-hot and evolving chlorine, chloric oxide, nitrogen, and a small quantity of oxygen gas. (Soubeiran.) When evaporated with hydrochloric acid, it is resolved into sal-ammoniac and bisulphate of ammonia. Becomes somewhat moist on exposure to the air; dissolves in 2 parts of cold, and in 1 part of boiling water.

β. BISULPHATE. Crystallizes in thin rhombohedrons or in scales; has an acid and bitter taste. Deliquesces slowly in the air. Dissolves in one part of cold water. (Link, *Crell. Ann.* 1796, 1, 25.)

The powder of *a* absorbs the vapour of anhydrous sulphuric acid very slowly and sparingly at ordinary temperatures; the compound fuses at a slightly elevated temperature, and when strongly heated is decomposed like bisulphate of ammonia. (H. Rose, *Pogg.* 38, 122.)

o. SULPHOCARBONATE OF AMMONIA.

Bisulphide of carbon slowly absorbs ammoniacal gas and is converted into a slightly yellow, amorphous powder, which in the anhydrous state is capable of being sublimed; it absorbs water greedily, assuming first an orange-yellow (arising from hydrosulphocarbonate of ammonia) and then a lemon-yellow colour, and is converted into ammonia, hydrosulphuric acid, and carbonic acid. (Berzelius & Marcet.) This compound is also formed on heating xanthonate of ammonia. (Zeise, *Pogg.* 35, 511.)

p. Hydro-sulphocarbonate of Ammonia.

The Chamelion Salt (*Rothwerdendes Salz*) *of Zeise*; *Sulphocarbonate of Ammonia*. (Berzelius.)—*Formation* (p. 206). 10 measures of alcohol saturated with ammoniacal gas are mixed with one measure of bisulphide of carbon; the mixture placed in ice-cold water, as soon as it has assumed a brownish yellow colour; and the mother-liquor, after standing for an hour, poured off from the crystallized salt (to prevent the latter from becoming contaminated with crystals of sulphocyanide of ammonium). The crystals are washed several times with alcohol and afterwards with ether, after which they are pressed rapidly between folds of bibulous paper, and preserved in a well stopped bottle.

The salt is pale yellow and crystalline. When exposed to the air it volatilises completely in the course of a few days. If kept from moisture, it may be sublimed almost unchanged; a small quantity of hydrosulphate of ammonia appears, however, to be formed during the process.

The salt when moistened with alcohol and exposed to the air instantly assumes a deeper yellow, and in a few seconds a red colour; if it has been well washed with ether and carefully pressed dry, it retains its yellow colour in the air for five minutes, and in well closed vessels for a still longer time. The aqueous solution loses its colour in the air, and deposits a grey precipitate containing carbon, but without formation of sulphocyanogen. An aqueous solution of potash distilled to dryness with the salt, gives a residue of sulphocyanide of potassium. When treated with milk of lime, it yields a large quantity of a yellow powder, together with a solution which still contains hydrosulphocarbonic acid. Hydrochloric and sulphuric acid instantly decolorize the red aqueous solution of this salt, and render it milky by separating hydrosulphocarbonic acid (an excess of the stronger acids, however, redissolves the precipitate); moreover, if the aqueous solution is concentrated, hydrosulphuric acid is also evolved, and a substance resembling sulphur separated. Moderately dilute hydrochloric or sulphuric acid separates pure hydrosulphocarbonic acid from the dry salt, without disengaging hydrosulphuric acid (p. 206). When left in closed vessels in contact with alcohol, the salt is resolved into hydrosulphuric acid and hydrosulphocyanate of ammonia.

$$2(NH^3, HCS^3) = NH^3, H^2C^2NS^2 + 3HS.$$

The salt attracts moisture from the air, and dissolves in water very readily and abundantly. One part of the salt imparts to 8 parts of water a red, to a larger proportion a brown, and to a still larger quantity a yellow colour. In close vessels, the solution remains unchanged for a very long time, excepting that the red colour changes to reddish brown. It is sparingly soluble in alcohol, and even less soluble in ether. (Zeise, *Schw.* 41, 105.)

q. Sulpho-phosphate of Ammonia.

Tersulphide of phosphorus (prepared with 31·4 parts of phosphorus and 48 parts of sulphur) slowly absorbs ammoniacal gas; the absorption does not terminate before the end of six months. The compound is solid, yellowish, and of hepatic taste; when heated, it softens without fusing, and gives off hydrosulphuric acid and hydrosulphate of ammonia; after which, sulphide of phosphorus sublimes, leaving phosphide of nitrogen in

the form of a porous mass. The compound becomes moist when exposed to the air and gives off an odour of ammonia and hydrosulphuric acid. When treated with water it yields phosphite of ammonia and a compound of sulphide of phosphorus with hydrosulphate of ammonia. (Bineau, *Ann. Chim. Phys.* 70, 265.)

	Calculation.		Bineau.
NH^3	17·0	17·63	17·5
P	31·4	32·58	32·6
3S	48·0	49·79	49·9
NH^3,PS^3	96·4	100·00	100·0

Nitrogen and Selenium.

A. Monohydroseleniate of Ammonia.—*Selenide of Ammonium.*—One volume of seleniuretted hydrogen gas mixed with an excess of ammoniacal gas condenses 2 volumes of the latter, forming a white cloud which is deposited in the form of a white mass having the odour of seleniuretted hydrogen and of ammonia. (Bineau.) It is not crystalline, and in consequence of the air removing a small quantity of hydrogen, it acquires a pale red colour, and forms a red solution with water. (Berzelius.)

B. Bihydroseleniate of Ammonia.—*Selenide of Ammonium and Hydrogen.*—When the ammoniacal gas is in excess, the two gases condense in equal volumes and form a white crystalline mass which smells of hydroselenic acid and ammonia, and is less volatile than bihydrosulphate of ammonia. On exposing it to heat, selenium is separated. Both A and B are rapidly decomposed in the air, with separation of selenium. (Bineau, *Ann. Chim. Phys.* 67, 229.)

	Calculation.			Calculation.	
A. NH^3	17	29·31	B. NH^3	17	17·17
HSe	41	70·69	2HSE	82	82·83
NH^3,HSe	58	100·30	$NH^3,2HSe$	99	100·00

Ammoniacal gas and aqueous ammonia have no effect on selenium. When a mixture of selenide of calcium and sal-ammoniac is distilled, ammoniacal gas and selenium are evolved, and a red liquid is obtained having a strong hepatic odour, and producing a red turbid mixture when mixed with a large quantity of water. On exposure to the air, it is resolved into ammonia and water which escape, and selenium which is precipitated. (Berzelius.) Probably this liquid should be regarded as hydroselenite of ammonia, that is to say, as hydroseleniate of ammonia containing an additional quantity of selenium in solution.

C. Selenite of Ammonia.

a. Monoselenite.—Formed by dissolving selenious acid in a slight excess of concentrated solutionof ammonia, and leaving the solution to evaporate in a warm place. Four-sided prisms—oblique four-sided tables—and feathery crystals. When heated, it swells considerably and evolves water and ammonia, and afterwards water and nitrogen gas, together with a small quantity of quadroselenite of ammonia partly dissolved in the water, and partly sublimed in the anhydrous state; the residue consists of fused selenium. It deliquesces in the air.

b. Biselenite. Prepared by dissolving the salt *a* in water and leaving the solution to spontaneous evaporation, whereby ammonia is evolved. It forms needles which are permanent in the air.

c. QUADROSELENITE. Prepared either by evaporating a solution of *b* with the aid of heat, or by treating it with an acid. Uncrystallizable and deliquescent in the air. (Berzelius.)

NITROGEN AND IODINE.

IODIDE OF NITROGEN? or IODIDE OF AMIDOGEN? NI^3, or NI or NH^2I?

Precipitated in the form of a black powder on mixing iodine or chloride of iodine with an aqueous solution of caustic ammonia or carbonate of ammonia. Either:

$$4NH^3 + 6I = 3(NH^3, HI) + NI^3; \text{ or:}$$
$$4NH^3 + 4I = 3(NH^3, HI) + NI; \text{ or:}$$
$$2NH^3 + 2I = NH^3, HI + NH^2I.$$

A small quantity of nitrogen gas is invariably disengaged during the process. A solution of iodate and hydriodate of ammonia yields a precipitate of iodide of nitrogen with potash, only when hydrochloric acid has been previously added. (Serullas.)—Iodide of nitrogen is also formed in the decomposition of chloride of nitrogen by a solution of iodide of potassium.

1. Powdered iodine is covered with an excess of aqueous ammonia, and the mixture promoted by gentle trituration in a mortar; the whole is then thrown on a filter and the hydriodate of ammonia washed out with cold water.—2. Alcohol of 33° Baumé is saturated with iodine, and the solution, after filtration or decantation, treated with a large excess of ammonia; the mixture is then stirred, diluted with water, and, after subsiding, poured off from the iodide of nitrogen produced. The new compound, which settles at the bottom of the vessel in the form of a black paste, is washed with cold water either by subsidence and decantation or on a filter, if it does not subside readily. The iodide of nitrogen thus produced has the form of a very fine powder, which, as long as it remains moist, does not explode even when pressed with a glass rod; whereas that which is prepared by the first method often explodes spontaneously even during washing. But if the iodine is precipitated from the alcoholic solution by water, and then ammonia added, spontaneously explosive iodide of nitrogen is obtained. (Serullas.)—3. Iodine is dissolved in hot aqua regia, and the solution, which contains terchloride of iodine, decanted from the undissolved iodine. On adding an excess of ammonia to the solution, iodide of nitrogen is precipitated in the form of a blackish brown powder. In this case, hydrochloric acid and iodide of nitrogen appear to be the only products, inasmuch as no nitrogen gas is evolved, and the liquid contains nothing but sal-ammoniac with the merest trace of hydriodate of ammonia. (Mitscherlich.) Hence it may be inferred that iodide of nitrogen = NI, since:

$$NH^3 + ICl^3 = NI + 3HCl.$$

The compound may also be prepared by mixing ammonia with aqueous solution of terchloride of iodine, or with a mixture of iodic acid and hydrochloric acid. (André, *J. Pharm.* 22, 137.)

The iodide of nitrogen, after being washed, is dried by exposure to the air at ordinary temperatures; but even when thus treated, it often explodes spontaneously. It is best to divide the filter with the moist iodide of nitrogen upon it into small pieces, and expose these to the air at considerable distances from each other, so as to preclude the possibility of a dangerous explosion. In a receiver full of ammoniacal gas, it may be

dried without fear of explosion, and kept for six weeks or more, and even touched without exploding, provided it has not previously been exposed to the air again. (Millon.) Bineau (*Ann. Chim. Phys.* 70, 270) also places hydrate of potash under the jar filled with the ammoniacal gas. The water adhering to the iodide of nitrogen at first absorbs ammoniacal gas; but after the iodide of nitrogen has become perfectly dry, the ammoniacal gas regains its original volume; so that the iodide is rendered less explosive without absorbing ammonia:

Iodide of nitrogen forms a brownish black, soft powder.

Calculation *a*, according to Gay Lussac.

N	14	3·57
3I	378	96·43
NI^3	392	100·00

Calculation *b*.

N	14	10
I	126	90
NI	140	100

Calculation *c*, according to Millon.

N	14	9·86
2H	2	1·41
I	126	88·73
AdI	142	100·00

Calculation *d*, according to Bineau.

N	14	5·23
H	1	0·37
2I	252	94 40
NHI^2	267	100·00

According to Bineau's view, this substance is formed from ammonia by the substitution of 2 atoms of iodine for 2 atoms of hydrogen. (*N. Ann. Chim. Phys.* 15, 71.)

Decompositions. Dry iodide of nitrogen explodes from the slightest cause, producing a loud report, and destroying any solid bodies lying near it. The explosion is attended with a violet light visible in the dark, the nitrogen being set free in the form of gas, and the iodine as a very fine powder. It explodes when merely dried in the air, and with greater readiness as the temperature of the air is higher. The slightest movement, or a gentle blow, the least elevation of temperature, or the addition of oil of vitriol or any other strong acid, whereby heat is probably disengaged, causes it to explode. Iodide of nitrogen when moist, or when placed under water, does not generally explode unless strongly rubbed. Oils and other fatty bodies do not cause it to explode. Besides the red vapour observed during the explosion, and consisting of finely divided iodine, a white vapour is also disengaged, probably hydriodate of ammonia; the light is occasioned by the union of hydrogen with iodine:

$$2(NH^2I) = NH^3, HI + I + N. \quad \text{(Millon).}$$

If portions of iodide of nitrogen as dry as possible and weighing 0·05 grm. each be repeatedly exploded under the same glass jar, traces of hydriodate of ammonia appear on the sides of the vessel; this seems to indicate the presence of hydrogen in the compound. (Marchand, *J. pr. Chem.* 19, 1.)

2. Iodide of nitrogen gradually dissolves under water, giving off small quantities of nitrogen, and forming iodate and hydriodate of ammonia; the solution is neutral and contains free iodine. (Serullas, Millon.) At ordinary temperatures, the solution is completed in a few days, more rapidly with the aid of heat, and in a few minutes if the water contains sulphuric or nitric acid; but the iodide of nitrogen prepared by the first method—not that prepared by the second—explodes slightly in hot water or acidulated water; moreover, with the latter it does not yield any hydriodic acid. (Serullas.) Were the compound $= NI^3$, an excess of acid should be produced:

$$NI^3 + 5HO = NH^3 + 2HI + IO^5;$$

the decomposition may, however, be explained according to calculation c:

$$3(NH^2I) + 5HO = 2(NH^3, HI) + NH^3, IO^5 \text{ (Millon)};$$

and also according to calculation b:

$$3NI + 10HO = NH^3, HI + 2(NH^3IO^5).$$

But inasmuch as indefinite quantities of nitrogen and iodine are set free during the decomposition, and the proportion of the iodate of ammonia to the hydriodic acid has not been ascertained, no decided conclusion can be arrived at. When dilute hydrochloric acid is gradually added to iodide of nitrogen under water, the iodide dissolves completely without evolution of gas, and the solution contains ammonia in combination with hydrochloric, hydriodic, and iodic acids. If caustic potash or carbonate of potash be then added in very slight excess, iodide of nitrogen again separates, because the ammonia set free by the potash reproduces iodide of nitrogen with the two acids of iodine present; the iodide of nitrogen in this manner may be repeatedly dissolved in hydrochloric acid and precipitated by potash. (Serullas.) Nevertheless, it diminishes after each precipitation, in consequence of nitrogen gas being evolved and iodine separated. (Millon.) If 6 drops of strong hydrochloric acid are poured upon 2 grammes of well washed iodide of nitrogen, the resulting liquid has no acid reaction, all the three acids, namely, hydrochloric, hydriodic and iodic acid, being saturated with ammonia. (Millon.)

3. Iodide of nitrogen is almost instantly decomposed by sulphuretted hydrogen water, with separation of sulphur, but no disengagement of gas; the resulting solution contains hydriodate of ammonia with a slight excess of hydriodic acid, derived from free iodine mixed with the iodide of nitrogen. (Serullas).—According to calculation a, a very acid liquid should be obtained:

$$NI^3 + 6HS = NH^3, 3HI + 6S;$$

but, according to calculation b or c, a neutral solution should be formed:

$$NI + 4HS = NH^3, HI + 4S; \text{ and}$$
$$NH^2, I + 2HS = NH^3, HI + 2S.$$

4. Solution of potash or milk of lime slowly added to iodide of nitrogen under water, dissolves it with evolution of ammonia, and formation of iodate of potash [and iodide of potassium?]. A mere trace of nitrogen is evolved at the same time—more, however, if the solution of potash is concentrated, because a rise of temperature then takes place. (Serullas.)

According to a: $NI^3 + 3KO + 3HO = 2KI + KO, IO^5 + NH^3$;
According to b: $3NI + 3KO + 9HO = KI + 2(KO, IO^5) + 3NH^3$;
According to c: $3NH^2, I + 3KO + 3HO = 2KI + 2KO, IO^5 + 3NH^3$.

B. *a*. Iodide of Ammonia?

Dry iodine absorbs dry ammoniacal gas: 100 parts of iodine take up 8·3 parts at + 10°; 9 parts at 0°; and 9·4 parts at −18°; at 0° and above, but not at −18°, a small quantity of nitrogen gas is set free, in consequence of the rise of temperature produced by the absorption. (Millon).—100 parts of iodine absorb 20·55 parts of ammonia. (Bineau, *Ann. Chim. Phys.* 67, 226.) Combination is also effected by gently heating iodine with sesquicarbonate of ammonia, water and carbonic acid being disengaged. (Colin, Bineau.)

Blackish-brown, very tenacious liquid, having a metallic aspect; the lustre and tenacity are destroyed by excess of ammonia. When heated, it evolves a portion of ammonia, and then sublimes undecomposed in violet-coloured vapours. (Gay-Lussac.)—The compound smells of iodine and ammonia, and imparts a brown stain to the skin and to paper. A large quantity of ammonia renders it as fluid as water, but on exposure to the air, it again becomes thick. (Landgrebe, *Schw.* 52, 100.)

Calculation, according to Millon.			Calculation, according to Bineau.		
NH^3	17	11·89	$3NH^3$	51	18·02
I	126	88·11	2I	232	81·28
NH^3I	143	100·00	$3NH^3, I^2$	283	100 00

According to Millon, it is a compound of one atom of iodide of amidogen, (the so-called iodide of nitrogen,) with one atom of hydriodate of ammonia;

$$2(NH^3, I) = NH^2, I + NH^3, HI.$$

This view is supported by the following statement of Millon, viz.: that from a small quantity of iodide of ammonia, a large quantity, having the same properties, may be prepared, by adding to the iodide of ammonia, first a small quantity of iodide of amidogen, which shortly dissolves, then powdered hydriodate of ammonia, which accelerates the solution, then iodide of amidogen again, and so on.

Water converts iodide of ammonia into aqueous hydriodate of ammonia and insoluble iodide of nitrogen. (Gay-Lussac.) A current of hydrochloric acid gas converts it into nitrogen gas, sal-ammoniac, hydriodate of ammonia, and free iodine. (Millon.) Iodide of ammonia dissolves readily in alcohol.

b. Hydriodate of Ammonia.

Iodide of Ammonium.—The two gases condense in equal volumes.—Caustic ammonia or carbonate of ammonia, is saturated with an aqueous solution of hydriodic acid; or a solution of iodide of iron is precipitated by carbonate of ammonia, and the liquid filtered.—The solution obtained in the preparation of iodide of nitrogen also contains this salt.—It appears to crystallize in cubes, and is colourless.—It volatilizes undecomposed out of contact of air, but when air is present, it yields a sublimate coloured yellow from excess of iodine.—At ordinary temperatures, it absorbs the vapour of anhydrous sulphuric acid and is decomposed, giving off sulphurous acid and forming a reddish-brown mass. (H. Rose).—Extremely deliquescent; easily soluble in water and alcohol. The solution acquires a yellow colour in the air, the salt being partially converted into the following compound, from oxidation of hydrogen in the hydriodic acid, and volatilization of ammonia.

Calculation.				Volume.
NH^3	17	11·81	Ammoniacal gas	1
HI	127	88·19	Hydriodic acid gas	1
NH^3HI	144	100·00		

c. Hydriodite of Ammonia.

Periodide of Ammonium.—An aqueous solution of iodide of ammonium saturated with iodine, forms a dark brown, nearly opaque liquid.

d. Iodate of Ammonia.

An aqueous solution of iodic acid or terchloride of iodine is neutralized with caustic ammonia or carbonate of ammonia. The salt separates in the form of a sparingly soluble crystalline powder. By slowly evaporating the solution, it may be obtained in very brilliant colourless cubes.—The crystals do not lose weight when slightly heated, but at 150°, they are decomposed with a hissing noise, evolving a mixture of oxygen and nitrogen gases in equal volumes, together with vapour of iodine and water. (Rammelsberg.)

$$NH^3, HO, IO^5 = 4HO + I + N + 2O.$$

—When thrown on ignited charcoal it explodes violently, with evolution of violet-coloured vapours. (Vauquelin.) With hydrochloric acid, it yields water, free chlorine, and a compound of sal-ammoniac with terchloride of iodine. (Filhol.) Dissolves in 38·5 parts of water at 15°, and in 6·9 parts of boiling water. (Rammelsberg, *Pogg.* 44, 555.)

	Calculation.		Rammelsberg.
NH^3	17	8·86	
IO^5	166	86·46	15·987
HO	9	4·68	
Crystallized	192	100·00	

Nitrogen and Bromine.

A. Bromide of Nitrogen? or Bromide of Amidogen?—An aqueous solution of bromide of potassium is added drop by drop to chloride of nitrogen covered with a thin stratum of water. The yellow colour of the chloride of nitrogen changes, on the addition of the bromide, into a red, which continues to increase in depth.—Dense, blackish-red, very volatile oil, the vapour of which has an offensive odour, and attacks the eyes very strongly.—Explodes violently by contact with phosphorus and arsenic.—When kept under water, it becomes covered with a bubble of nitrogen gas, which increases, bursts, and is again formed, till the compound entirely disappears; the water at the same time dissolves hydrobromate of ammonia, with excess of bromine. Aqueous solution of ammonia decomposes the oil, producing dense white fumes. (Millon, *Ann. Chim. Phys.* 69, 75.)

B. Hydrobromate of Ammonia.—*Bromide of Ammonium.*—The two gases condense in equal volumes. Aqueous solution of ammonia is saturated with hydrobromic acid and the liquid evaporated.—Long, colourless crystals, having a sharp, saline taste; when heated, they evaporate without previously fusing.—When exposed to the air, this compound becomes slightly yellow, and acid to litmus paper, from formation of a small quantity of hydrobromite of ammonia. (Balard.) It dissolves readily in water, very sparingly in alcohol.

	Calculation.		Volume.	
NH^3	17·0	17·63	Ammoniacal gas	1
HBr	79·4	82·37	Hydrobromic acid gas	1
NH^3,HBr.	96·4	100·00		

C. Bromate of Ammonia.—Formed by saturating aqueous solution of ammonia with aqueous bromic acid, or by precipitating bromate of baryta by carbonate of ammonia, and filtering the solution. Colourless

needles and grains of a very pungent and cooling taste. (Löwbig.) Explodes violently, not only when gently heated, but even at ordinary temperatures, after a short time, so that it cannot be kept in the solid state. The products of decomposition are water, bromine vapour, nitrogen, and oxygen. (Rammelsberg, *Pogg.* 52, 85.)

D. AMMONIO-TERBROMIDE OF PHOSPHORUS.—Terbromide of phosphorus absorbs ammoniacal gas, with great disengagement of heat. If, however, the rise of temperature be prevented by surrounding the bromide of phosphorus with a freezing mixture and passing the ammoniacal gas very slowly into it, a white powder is obtained, which, when ignited in a current of carbonic acid gas, is resolved into between 13·24 and 13·81 per cent. of phosphide of nitrogen, together with hydrobromate of ammonia, vapour of phosphorus, ammoniacal gas, and hydrogen. The compound dissolves slowly but completely in water, yielding a solution of phosphite and hydrobromate of ammonia.

$$5NH^3, PBr^3 + 3HO = 2NH^3, PO^3 + 3(NH^3, HBr.)$$

(H. Rose, *Pogg.* 28, 549.)

	Calculation.		H. Rose.
$5NH^3$	85·0	24·17	
P	31·4	8·93	
3Br	235·2	66·90	66·9
$5NH^3, 3PBr^3$	351·6	100·00	

NITROGEN AND CHLORINE.

A. *a.* CHLORIDE OF NITROGEN? OR CHLORIDE OF AMIDOGEN?

Chlor-Stickstoff, Halogenazot, Chlorure d'azote.—The composition of this explosive oil is involved in as much uncertainty as that of iodide or bromide of nitrogen; it is, however, analogous to these compounds, inasmuch as it yields iodide of nitrogen and chloride of potassium with an aqueous solution of iodide of potassium, and bromide of nitrogen and chloride of potassium with bromide of potassium. As in the case of iodide of nitrogen, *a* may represent the assumption that chloride of nitrogen is NCl^3; *b*, that it is NCl, and *c*, that it is NH^2, Cl.

Formation.—1. When chlorine is made to act on free ammonia or a compound of ammonia with a weak acid dissolved in water, sal-ammoniac is formed and all the nitrogen is set free (p. 423),—or if any chloride of nitrogen be formed, it is rapidly decomposed; but if the ammonia is combined with a stronger acid, as phosphoric, sulphuric, hydrochloric, nitric, or oxalic acid, which in some measure protect the ammonia from the decomposing influence of the chlorine, the latter not only unites with the hydrogen of the ammonia, whereby free hydrochloric acid is formed, but a portion of it combines at the same time with the nascent nitrogen (or with the amidogen), and produces the explosive oil. According to theory *a*, the sal-ammoniac is decomposed in the following manner:

$$NH^3, HCl + 6Cl = 4HCl + NCl^3; \ (Sch.\ 38);$$

according to theory *b*:

$$NH^3, HCl + 4Cl = 4HCl + NCl;$$

according to theory *c*:

$$NH^3, HCl + 2Cl = 2HCl + NH^2, Cl.$$

The formation of the oil is not attended by any sensible rise of temperature. (Dulong.) It is effected more rapidly at + 32° C. and above, than at ordinary temperatures; below 0° it does not take place at all; it is also prevented when the solution of the ammoniacal salt contains hydrosulphite of ammonia (NH^3, HS^3), or when it is mixed with powdered sulphur or powdered charcoal, or when the chlorine gas is mixed with a third of its volume of air or carbonic acid gas, or with an equal volume of hydrogen gas. (Porret, Wilson, & Kirk.)—2. An aqueous solution of hypochlorous acid produces the explosive oil, both with solutions of the ammoniacal salts and with free ammonia. (Balard.)

Preparation.—1. Chlorine gas is passed through the solution of a suitable ammoniacal salt at a temperature of + 8° (46·4° F.). (Dulong.) Berzelius fills a glass jar with solution of sal-ammoniac, inverts it in a dish filled with the same solution, and passes chlorine gas into the jar.—2. A bottle of the capacity of 16 cubic inches is filled with chlorine gas over hot water and inverted in a dish containing solution of sal-ammoniac at a temperature of 32° C. (89·6° F.) (Porret, Wilson, & Kirk.) The oil produced first saturates the chlorine with its vapour, then forms a film on the sides of the vessel and over the liquid, and finally sinks to the bottom in the form of drops. Serullas inverts the jar filled with chlorine gas over a dish containing a lukewarm solution of one part of sal-ammoniac in 15 parts of water; pours more solution into the dish in proportion as it rises in the jar; and when the chlorine has entirely disappeared, cautiously removes the jar, so as to prevent the oil from attaching itself to the surface, and thereby forming a film which would rapidly volatilize in the air. He then inclines the dish containing the oil and passes a continuous stream of lukewarm water over it, in such a manner that the oil may be constantly covered with water; this is continued till the water which runs off no longer forms a cloud with solution of silver.—3. A piece of sal-ammoniac or of sulphate of ammonia is suspended in an aqueous solution of hypochlorous acid; the oily drops are deposited, and small quantities of nitrogen and chlorine are evolved. (Balard.)

The preparation and handling of this body require the greatest caution. The glass jar must be freed from every trace of fat by treatment with potash and water, as even the grease from the fingers may cause an explosion. Explosion often takes place spontaneously, without any apparent cause. In all experiments with this substance, thick gloves and a strong mask with thick pieces of glass before the eyes are indispensable. It is preserved in sealed glass tubes, with some watery liquid placed above it.

Properties. Thin oil of the colour of wax, and of specific gravity 1·653; does not freeze at a temperature near—40°. (H. Davy.) Volatilizes rapidly in the air. May be distilled at a temperature below + 71° (160° F.). Does not appear to conduct electricity. (Porret, Wilson, & Kirk.) Has a peculiar pungent odour, and makes the eyes smart; its action on the lungs is less powerful than that of chlorine.

	Calculation *a*.		Bineau.
N	14	11·65	10·6
3Cl	106·2	88·35	89·3
NCl^3	120·2	100·00	100·0

Calculation *b.*			Calculation *c.*		
N	14	28·34	NH^2	16	31·13
Cl	35·4	71·66	Cl	35·4	68·87
NCl	49·4	100·00	NH^2, Cl	51·4	100·00

According to Sir H. Davy, it is NCl^4; according to Porret, Wilson, & Kirk, $NHCl^3$; according to Millon (*Ann. Chim. Phys.* 69, 75), it is a compound of nitride of chlorine with ammonia, Cl^3N+2H^3N. Bineau regards it as ammonia, the hydrogen of which is wholly replaced by chlorine (*N. Ann. Chim. Phys.* 15, 71).

Decompositions. Many circumstances cause chloride of nitrogen to explode with great violence, producing a flashing light and loud report, and often shattering the containing vessel in pieces. A grain and a half of the oil produces a report louder than the discharge of a gun.—The explosion is induced either by direct elevation of temperature to at least 93° (about 200° F.), as when a red-hot iron is brought in contact with the vapour, &c., or by touching the liquid with substances which unite with a portion of the chlorine, the combination being attended with rise of temperature. An extremely violent explosion is caused by phosphorus; and also, according to Serullas, by selenium or arsenic in the form of powder; somewhat less powerful explosions are produced by phosphide of calcium, phosphorus dissolved in bisulphide of carbon, phosphuretted hydrogen gas (which at the same time disappears) sulphuretted hydrogen gas, persulphide of hydrogen, nitric oxide gas, strong aqueous ammonia; lead-paint, manganese, the compounds (soaps) of margaric and oleic acid with the oxides of manganese, copper, silver, and mercury; rock oil, the oils of amber, turpentine, and orange, phosphuretted camphor, palm-oil, train-oil, olive-oil, camphorated olive-oil, linseed-oil, amber, myrrh, caoutchouc.—Hydrate of potash likewise causes explosion when water is present, in consequence of the heat disengaged when it dissolves. (Porret, Wilson & Kirk.) Cyanide of potassium also causes explosion, whether in the solid state or in the form of a concentrated solution. (Millon.)

2. The following substances effect a gradual decomposition of chloride of nitrogen, generally accompanied by effervescence and the disengagement of nitrogen gas, sometimes also of chlorine gas.

When kept under cold water, chloride of nitrogen disappears in the course of 24 hours, nitrogen and chlorine gases being evolved and hydrochloric and nitric acid formed. (H. Davy, Serullas.)

Sulphuretted hydrogen water deposits milk of sulphur, with slight evolution of nitrogen gas, and gives a solution of sal-ammoniac, in which the hydrochloric acid is slightly in excess, in consequence of the separation of nitrogen which has taken place. (Serullas.) [The fact of the solution being nearly neutral can be explained only by the theory *b*, or *c*; according to the theory *a*, 3 atoms of hydrochloric acid should be formed to 1 atom of ammonia.]

Concentrated hydrochloric acid gradually converts the oil into hydrochlorate of ammonia, disengaging a quantity of chlorine gas, greater than the original weight of the oil; 1 grain evolves at most 3·9 cubic inches of chlorine gas; a portion of chlorine likewise remains dissolved in the hydrochloric acid. (H. Davy.) [An instance of reciprocal affinity; since chlorine and sal-ammoniac form hydrochloric acid and the explosive oil, and the latter is again resolved by concentrated

hydrochloric acid into sal-ammoniac and chlorine.] According to *a*: $NCl^3+4HCl = NH^4Cl + 6Cl$;—according to *b*: $NCl+4HCl = NH^4Cl + 4Cl$;—according to *c*: $NH^2Cl+2HCl = NH^4Cl+2Cl$.

Under dilute sulphuric acid, the oil disappears, with evolution of nitrogen and oxygen gases; under concentrated nitric acid, with evolution of nitrogen gas. (Sir H. Davy.)

With dilute ammonia, it evolves nitrogen gas and forms nitric acid. (H. Davy.)

Dilute solution of potash gives rise to the formation of hydrochlorate and nitrate of potash, with evolution of nitrogen gas. The oxides of lead, cobalt, copper, and silver likewise disengage nitrogen gas, and form chlorides and nitrates. (Serullas.)

Copper or mercury placed in contact with the oil under water, disengages nitrogen gas and yields a metallic dichloride and protochloride of the metal. (Dulong, H. Davy.) When chloride of nitrogen is passed up an inverted tube filled with mercury, 2 grains are sufficient to cause explosion; but a smaller quantity is quietly decomposed, a mixture of dichloride and protochloride of mercury being formed, and nitrogen gas evolved, amounting in quantity to 9 per cent. of the chloride of nitrogen employed. (H. Davy.)

A solution of nitrate of silver sometimes disengages nearly 2 measures of chlorine to 1 of nitrogen, chloride of silver being precipitated, and nitric acid formed at the same time. (Serullas.)

Arsenious acid rapidly produces ammonia, and causes partial volatilization of the oil. (Serullas.)—The oil separates arsenic from arseniuretted hydrogen. (Porret, &c.)

An aqueous solution of monosulphide of potassium produces a greenish-coloured powder, which floats on the surface of the liquid.—An aqueous solution of bromide or iodide of potassium converts chloride of amidogen into bromide or iodide of amidogen and chloride of potassium. (Millon.)

A moderately-concentrated solution of cyanide of potassium yields with chloride of amidogen—chloride of potassium and a white cloud probably consisting of cyanide of amidogen; a dilute solution disengages nitrogen gas only.—Sulpho-cyanide of potassium, either in the solid or liquid state, produces an orange-coloured buttery mass, which dissolves in excess of the sulpho-cyanide. (Millon.)

The following substances also give rise to the gradual decomposition of chloride of nitrogen, with slight effervescence: lime, carbonate of lime, red-lead; the soaps formed by the combination of baryta, strontia, lime, and magnesia, with margaric and oleic acid; common resin, ox-gall resin;—and with rapid effervescence, the soaps formed with potash, alumina, tin, and cobalt; and the solutions of phosphorus in ether, and of resin or shellac in alcohol. (Porret, Wilson & Kirk.)

The following substances exert no decomposing action on chloride of nitrogen: sulphur, bi-sulphide of carbon; dilute phosphoric, sulphuric, hydrochloric, and nitric acids; ferro-cyanide of potassium; tin, zinc, native sulphide of antimony, cinnabar, charcoal, jet; shellac, frankincense, scammony, aloes, gum-ammoniac, wax, spermaceti, stearine, butter, lard, alcohol, sulphuric ether, nitrous ether, sugar, manna, gum, starch, indigo, gum-kino, catechu, dried white of egg, and benzoic acid.—Chloride of nitrogen may likewise, to all appearances, be evaporated in oxygen, hydrogen, nitrogen, olefiant gas, and atmospheric air, without being decomposed. (Porret, Wilson & Kirk.)

Combinations.—*a.* Sulphur, when added in small portions to the oil, is quietly dissolved. (Serullas.) According to Dulong, sulphur decomposes chloride of nitrogen, producing a compound which rapidly dissolves in water, and forms a solution of hydrochloric and sulphuric acids.

b. With bisulphide of carbon, chloride of nitrogen forms a yellow mixture which does not explode with phosphorus or fatty oils, but quietly sets fire to an excess of these substances. (Porret, &c.) A mixture of chloride of nitrogen and bisulphide of carbon, is slowly decomposed under water, into nitrogen gas, ammonia, hydrochloric acid, and sulphuric acid; the addition of phosphorus to the mixture causes violent ebullition. (Serullas.)

c. The oil dissolves in terchloride of phosphorus and in chloride of sulphur. (H. Davy.)

d. With numerous organic substances: the combination is, however, in most instances attended with effervescence, and consequently with partial if not total decomposition. Thus it combines with asphalt, elaterite, copal, mastic, guiacum, euphorbium, asafœtida, camphor, sulphuretted camphor, oil of musk, stearic and oleic acids, olive-oil, palm-oil and oil of turpentine, when chlorine is made to pass through them, and with olive oil which has been boiled over corrosive sublimate. (Porret, Wilson & Kirk.)

b. Chlorophosphide of Nitrogen. $N^2P^3Cl^5$.

Formed by the action of pentachloride of phosphorus on ammonia or sal-ammoniac.—1. Pentachloride of phosphorus is saturated with moist ammoniacal gas, and the white mass produced is distilled with water. The crystals which condense in the water contained in the receiver are then collected on a filter, washed, dried, and purified by solution in hot ether and re-crystallization.—2. Pentachloride of phosphorus is placed at the closed end of a glass tube 3 feet in length, and at a short distance from it, long pieces of sal-ammoniac are introduced, in such quantity that the tube may be half filled with them. The tube is then laid horizontally in a long furnace, similar to that used for organic analysis, and the sal-ammoniac first heated till it begins to volatilise; a gentle heat is then applied to the chloride of phosphorus, so that its vapour may slowly pass over the sal-ammoniac, and be completely decomposed. A large quantity of hydrochloric acid gas is evolved, and the cool part of the tube becomes filled with crystals of chlorophosphide of nitrogen. This portion of the tube is broken off, and freed from sal-ammoniac by slightly washing it with water. The new compound is finally purified with ether.

Large, colourless, transparent, regular, six-sided prisms, brittle, easily pulverized; not moistened by water, like grease; fuse below 100°, and form a transparent colourless liquid, which at a higher temperature boils and sublimes unchanged; when slightly heated, it exhales a peculiar but not pungent odour.

	Calculation.		Wöhler & Liebig.
2N	28·0	9·36	10·3
3P	94·2	31·49	31·4
5Cl	177·0	59·15	58·3
$N^2P^3Cl^5$	299·2	100·00	100·0

When ignited with oxide of copper in a tube, this compound yields nitrogen gas and hyponitric acid. When its vapour is passed over red-hot iron, the products are nitrogen gas free from hydrogen, and a crystalline mass from which water extracts chloride of iron, and leaves black

pulverulent phosphide of iron. Alcohol and ether dissolve the compound with facility. Sulphuric, hydrochloric, and nitric acids and solution of potash neither decompose nor dissolve it; but on the application of heat, it swims on their surface in oily drops and sublimes. (Möhler & Liebig, *Ann. Pharm.* 11, 146.)

c. Chlorosulphide of Nitrogen. NS^3, SCl.

Sulphazotic Chloride of Sulphur, Chlorosulphure azotique.

1. The compound of one atom of chloride of sulphur with one atom of ammonia (p. 485) heated in a glass tube for some hours at a temperature of 100°, is converted (without further alteration) into a yellow mixture of sal-ammoniac and chlorosulphide of nitrogen.

$$4(NH^3, SCl) = 3(NH^3, HCl) + NS^4Cl.$$

This mixture has a peculiar odour. When strongly heated it gives off sal-ammoniac, and is likewise resolved, into nitrogen gas, chloride of sulphur, and sulphur.

$$NS^4Cl = N + S^2Cl + 2S.$$

It dissolves perfectly in water; the solution, which has a peculiar smell, and at first a yellow colour, becomes turbid after a while, and slowly deposits a brown powder. The now colourless solution contains ammonia, hydrochloric, hyposulphurous, sulphuric acid, and a trace of hydro-sulphuric acid; but no sulphuric acid is formed, as long as the liquid continues yellow. If the small quantities of the insoluble brown powder, sulphur, and sulphide of nitrogen are disregarded, the decomposition will be as follows:

$$NS^4Cl + 4HO = NH^3, HCl + 2S^2O^2. \text{ (Soubeiran.)}$$

The brown powder, after being washed with water till no more chlorine is removed, then with cold alcohol, and lastly with boiling ether—which dissolves out sulphide of nitrogen together with a small quantity of sulphur and traces of chlorine—and afterwards dried in vacuo, behaves in the following manner: when heated, it evolves equal measures of nitrogen and ammoniacal gas, and leaves a large quantity of sulphur. It dissolves slowly in water, yielding a solution of hyposulphite of ammonia with a small quantity of sal-ammoniac, and depositing sulphur. It is insoluble in alcohol and ether; but if a piece of hydrate of potash is added to the alcohol, the compound dissolves, forming a fine amethyst-coloured solution, which gradually loses its colour, in consequence of the formation of hyposulphite of potash. Sulphide of sodium instead of hydrate of potash produces the same colour, but much paler. According to analysis, the powder contains about 7 atoms of sulphur, 3 atoms of nitrogen, and 3 atoms of hydrogen, with a trace of chlorine. (Soubeiran.) According to Bineau, (*Ann. Chim. Phys.* 70, 268) the same brown powder is obtained, mixed however with a large quantity of sulphur, when the compound of protochloride of sulphur with 2 atoms of ammonia is treated with water. The new compound dissolves in bisulphide of carbon much more abundantly than, sulphur, and crystallizes from the solution, on spontaneous evaporation, in brilliant brownish red crystals. According to the same authority, it contains one atom of nitrogen and one atom of hydrogen, combined apparently with 2 atoms of sulphur.

2. When dry carbonic acid gas is passed through a hot solution of sulphide of nitrogen in protochloride of sulphur, a small quantity of chlo-

rosulphide of nitrogen sublimes after a while in yellow crystals. The latter compound is characterized by giving a blue colour with ammonia. (Soubeiran, *Ann. Chim. Phys.* 67, 87, & 101; also *J. Pharm.* 24, 64, & 75.)

B. Aqua-Regia.

Nitromuriatic acid, Königswasser, Goldscheidewasser, Acide Nitro-muriatique.

Formation and Preparation.—By mixing aqueous nitric and hydrochloric acids; by dissolving a nitrate in aqueous hydrochloric acid; by dissolving a hydrochlorate or metallic chloride in aqueous nitric acid. In all these cases, the liquid gradually becomes yellow, but with peculiar rapidity when heated, because the hydrogen of the hydrochloric acid (*Sch.* 67) or of the metal in the metallic chloride, becomes oxidized, and chlorine and hyponitric acid are thereby produced. In a close vessel, the decomposition and separation of chlorine are arrested as soon as the liquid is saturated with the gas; but in an open vessel, from which the chlorine can escape as fast as it is evolved, the action continues till either the whole of the nitric acid or the whole of the hydrochloric acid or metallic chloride present is decomposed. (Berzelius.) If the liquid be heated till it disengages no more chlorine, it loses the power of dissolving gold. (H. Davy, *Quart. J. of Sc.* 1, 67; also *Gilb.* 57, 296). A mixture of hydrochloric acid gas and hyponitric acid vapour cannot be made to condense; aqueous hydrochloric acid may indeed be mixed with hyponitric acid, but the mixture does not dissolve gold. (H. Davy.) The usual proportions for aqua-regia are 1 part of nitric, and between 2 and 3 parts of hydrochloric acid.

Yellow, fuming, highly corrosive liquid, used for dissolving those metals in hydrochloric acid, which have but a feeble affinity for oxygen.—When metals are dissolved in aqua-regia, the nitric acid is almost entirely converted into nitric oxide gas. On the assumption that a metal—copper, for example—dissolves as chloride, we have:

$$3Cu + NO^5 + 3HCl = 3CuCl + 3HO + NO^2;$$

on the assumption that it dissolves in the form of hydrochlorate of the oxide:

$$3Cu + NO^5 + 3HCl = 3(CuO, HCl) + NO^2.$$

A mixture of hydrochloric acid of a certain degree of dilution, with nitric acid perfectly free from hyponitric acid, is not resolved at ordinary temperatures into chlorine and hyponitric acid, and consequently does not attack several of the metals, such as arsenic, antimony, platinum, &c. The action, however, commences on gently heating the mixture, or on adding a small quantity of nitrite of potash. Hence the presence of nitrous acid, whether it be produced by the mutual decomposition of the two acids on exposure to heat, or directly added to the mixture, is requisite for setting up the action on the metal. The addition of chlorine does not produce any effect. (Millon, *vid.* also pp. 398, 399.)

¶ The nature of aqua-regia has been further investigated by E. Davy and Baudrimont, and more lately by Gay-Lussac. According to E. Davy, the peculiar properties of aqua-regia are due to the presence of a compound which he calls *chloro-nitrous acid,* consisting of equal volumes of chlorine and nitric oxide: this compound is evolved as a gas of an

orange-yellow colour, when common salt or chloride of potassium is acted upon by strong nitric acid. Baudrimont (*J. Pharm.* 5, 49), by heating a mixture of 2 parts (by weight) of nitric acid and 3 of hydrochloric acid, to a temperature of 86° (177° F.), and passing the evolved gases through a cooled U-tube, for the purpose of condensing free hydrochloric acid, obtained a red gas which reddened moist litmus paper and bleached it after some hours, but had no effect on dry litmus paper. It attacked gold and platinum; arsenic and antimony took fire when thrown into it in the state of powder; on phosphorus, even when melted, it had no effect. When passed through a tube surrounded with ice and salt, it condensed to a liquid of a deep red colour, which, as well as the gas itself, dissolved readily in water. At the temperature of 0°, water took up 121 times its volume of the gas, forming a liquid of a bright red colour. This compound, which Baudrimont calls *chloro-nitric acid*, is composed, according to his analysis, of 1 atom of nitrous acid and 2 atoms of chlorine, NO^3, Cl^2; its formation may be expressed as follows:

$$NO^5 + 2HCl = NO^3Cl^2 + 2HO.$$

This, however, does not explain the evolution of free chlorine, which always takes place on heating a mixture of nitric and hydrochloric acids.

Gay-Lussac has shown that when the gases evolved from aqua-regia at the temperature of boiling water are passed through tubes surrounded with a freezing mixture, a cloudy, lemon-coloured liquid is obtained, whose composition is expressed by the formula, NO^2,Cl^2; it may be regarded as hyponitric acid, in which 2 atoms of oxygen are replaced by chlorine; it may therefore be called *Hypo-chloronitric acid.* Its formation is thus represented:

$$NO^5 + 3HCl = NO^2Cl^2 + 3HO + Cl.$$

and this accounts for the liberation of chlorine, which is an invariable concomitant of the action. Hypo-chloronitric acid is immediately decomposed by water, forming a solution which contains hydrochloric acid, but no free chlorine:

$$NO^2Cl^2 + 2HO = 2HCl + NO^4.$$

Hypo-chloronitric acid is not, however, the only product of the decomposition of aqua-regia by heat. The condensed product also contains another liquid, composed of 1 atom of nitric oxide and 1 atom of chlorine, NO^2Cl: this may be regarded as nitrous acid in which 1 atom of oxygen is replaced by chlorine: Gay-Lussac distinguishes it by the name of *Chloronitrous acid.* It may likewise be formed by allowing nitric oxide and chlorine to condense together in a vessel surrounded by a freezing mixture; but even then, the product is not a definite body; for the proportions of nitric oxide in the less volatile portions are much greater than in the more volatile. When common salt is heated with nitric acid, a mixture of hypochloric and chloronitrous acids is evolved, in various proportions depending upon the strength of the acid, the temperature, &c. When gold is acted upon by aqua-regia, the products of decomposition are exactly the same, viz., chloronitric vapour, water, and free chlorine; moreover, the chlorine alone is retained by the gold, while the chloronitric vapour passes off, just as when the liquid is simply heated. Hence it appears that the peculiar action of aqua-regia on metals, &c., is due to the free chlorine evolved in its decomposition. (Gay-Lussac, *Ann. Chim. Phys.* 33, 203; also *Ann. Pharm.* 66, 213; abstr. *Q. J. of Chem. Soc.* 1, 340.) ¶

C. *a.* HYDROCHLORATE OF AMMONIA.

Muriate of Ammonia, Chloride of Ammonium, Sal-ammoniac, Salsäures Ammoniak, Salmiak, Muriate d'Ammoniaque, Hydrochlorate d'ammoniaque, Chlorure d'Ammonium, Chlorure ammonique, Sal ammoniacum.

Found native near volcanos, on the burning mountain of Duttweiler (Glaser, *Kastn. Arch.* 14, 169), and, in very small quantity, in sea water and certain mineral waters.

Equal volumes of hydrochloric acid and ammoniacal gases rapidly condense into solid sal-ammoniac, the combination being attended with evolution of heat.

Preparation.—1. *Egyptian method of preparing Sal-ammoniac.* In Egypt, sal-ammoniac is sublimed from the soot obtained by burning camels' dung. (*Vid. Taschenb.* 1780, 53.)—2. *Liège method of preparing sal-ammoniac.* A mixture of coal, common salt, animal matter, and clay is burned in peculiarly constructed ovens, and the soot obtained in this manner is afterwards sublimed.—3. *European method of preparing sal-ammoniac.* The impure carbonate of ammonia obtained by the destructive distillation of solid animal matter, or by the distillation of putrid urine, is either directly converted into chloride of ammonium by treating it with hydrochloric acid, chloride of calcium, chloride of magnesium, or chloride of aluminum; or it is first converted into sulphate of ammonia by sulphuric acid, sulphate of iron, or gypsum, and the sulphate afterwards converted into chloride by means of common salt.—The salt is generally separated from the other substances by sublimation, whereby it is often obtained in grey or brown coloured cakes of a fibrous texture. It is purified either by a second sublimation on the small scale, or by solution in water, filtration, and crystallization; by the latter method it is obtained in fine crystals: *Flowers of Sal-ammoniac, Purified Sal-ammoniac.*

Properties. Regular octohedrons, cubes, trapezohedrons (*Fig.* 1, 2, 11) and feathery crystals. (*Vid.* Marx, *Schw.* 54, 299.) Sp. gr. = 1·450 (Wattson), 1·50 (Kopp), 1·528 (Mohs). Tough, difficult to powder. Does not volatilize at ordinary temperatures (Faraday); a small quantity, however, is evolved when the aqueous solution is boiled (Soubeiran, *J. Pharm.* 12, 242); when heated, it volatilizes undecomposed, and without previously fusing. [For the specific gravity of the vapour, *vid.* I., 280.] Permanent in the air; of a sharp saline taste; neutral.

Calculation.			Kirwan.	Bucholz.	Berzelius.		Vol.	Sp. gr.
NH^3	17·0	31·8	25	31	31·95	Ammoniacal gas	½	0·29465
HCl	36·4	68·2	75	69	68·05	Hydrochloric acid gas	½	0·63090
NH^3,HCl	53·4	100·0	100	100	100·00	Vapour	1	0·92555

Potassium heated with sal-ammoniac forms chloride of potassium and disengages 2 volumes of ammoniacal gas to 1 volume of hydrogen. (H. Davy.) Iron and other metals act in a similar manner, but less energetically. The resulting metallic chlorides frequently unite with the ammonia set free, or with undecomposed sal-ammoniac.—A mixture of sal-ammoniac and chlorate of potash is decomposed below the boiling point of oil of vitriol, evolving a gas which smells strongly of chlorine. (Soubeiran.) [For the decomposition of sal-ammoniac by chlo-

ride of phosphorus, *vid*. p. 437.] When exposed to the air, sal-ammoniac loses ammonia and becomes acid to test paper; if it be heated to the subliming point, then cooled and dissolved in cold water, it recovers its neutrality; but if dissolved in hot water, it loses ammonia and again acquires an acid reaction. (Emmet.) Upon this ready volatilisation of ammonia depends in part the power which an aqueous solution of sal-ammoniac (and other ammoniacal salts) possesses of dissolving insoluble carbonates and other salts.—One part of sal-ammoniac dissolves at 18·75° (65·75° F.), with great decrease of temperature, in 2·7 parts of water, forming a solution of specific gravity 1·08 (Karsten). From a saturated solution, strong hydrochloric acid precipitates a portion of the sal-ammoniac. (A. Vogel, *J. pr. Chem.* 2, 199.) Sal-ammoniac dissolves in about its own weight of boiling water; it is very sparingly soluble in alcohol.

Dry sal-ammoniac powder placed in a vessel surrounded with ice, absorbs the vapour of anhydrous sulphuric acid very abundantly and without disengagement of gas; the product is a translucent mass which is flexible at first, but afterwards becomes hard. The mass, when heated, first evolves hydrochloric acid gas, and then the products of decomposition of sulphate of ammonia. The addition of a few drops of water converts it, with violent evolution of hydrochloric acid gas, into ordinary sulphate of ammonia; a similar result is produced by exposure to moist air. The compound cannot be formed from anhydrous sulphate of ammon and hydrochloric acid gas. (H. Rose, *Pogg.* 38, 118;—*vid.* also Berzelius, *Jahresbericht*, 16, 139;—Kane, *Ann. Chim. Phys.* 72, 139.)—In the same manner, pure nitrate of potash absorbs anhydrous sulphuric acid at ordinary temperatures without disengaging nitric acid; hydrochlorate of ammonia possesses the same property.

b. Hypochlorite of Ammonia.

A mixture of very dilute hypochlorous acid and ammonia—even when the ammonia is in excess—decolorizes solution of sulphate of indigo, and continues to evolve bubbles of nitrogen till it is completely decomposed. (Balard.)—When a carefully prepared solution of chloride of lime is precipitated with a quantity, not quite sufficient for complete saturation, of a mixture of sesqui-carbonate of ammonia and enough caustic ammonia to prevent effervescence (or with phosphate or oxalate of ammonia), and the liquid decanted from the insoluble carbonate of lime, a similar solution is obtained. This liquid when heated, effervesces strongly, gives off bubbles of nitrogen gas, and becomes acid. The salt is also destroyed by evaporation in vacuo, sal-ammoniac alone remaining. (Soubeiran, *Ann. Chim. Phys.* 48, 141.)

¶ *c.* Chlorite of Ammonia.

Formed by saturating the aqueous solution of chlorous acid with ammonia. The solution bleaches vegetable colours, even when the ammonia is in excess. This salt has not been obtained in the solid state, for the solution cannot be concentrated without decomposition. (Berzelius, *Traité*, 3, 294.) ¶

d. Hypochlorate of Ammonia?

Aqueous solution of ammonia absorbs chloric oxide gas. The yellow liquid obtained continually evolves nitrogen gas and leaves chlorate of ammonia on evaporation. (Soubeiran, *Ann. Chim. Phys.* 48, 140.)

e. Chlorate of Ammonia.

1. Formed by mixing an aqueous solution of chloric acid with caustic ammonia or carbonate of ammonia. (Gay-Lussac.)—2. By precipitating chlorate of baryta, strontia or lime, with carbonate of ammonia. (Chenevix.)—3. By adding finely-divided chlorate of potash in small portions at at a time, to an aqueous solution of fluoride of silicium and ammonium, as long as fluoride of silicium and potassium continues to be formed—and then filtering the solution. (Berzelius).—The salt crystallizes in fine needles; has a very pungent taste. According to Vauquelin, it appears to volatilize below the boiling point of water.—When placed on a hot surface, it explodes a with red light, like burning nitre; if the salt is decomposed by a gentle heat, a mixture of chlorine, nitrogen, and a small quantity of oxygen, or more probably nitrous oxide gas, is obtained, a small quantity of sal-ammoniac, with excess of acid, remaining behind. (Vauquelin.) The crystals sometimes explode spontaneously when kept. (Mitscherlich, *Pogg.* 52, 85.)—Very soluble in water and alcohol. (Chenevix.)

f. Perchlorate of Ammonia.

Colourless, transparent prisms belonging to the right prismatic system (*Fig.* 53); in this figure, the prisms are supposed to be seen from above: $u : u = 103° 12'$; $y : y = 102° 5'$. (Mitscherlich, *Pogg.* 25, 300.) —It dissolves in 5 parts of cold water; the solution is neutral, but gives off ammonia when evaporated, and becomes acid; from the latter solution, concentrated perchloric acid precipitates the neutral salt by absorbing water. Sparingly soluble in alcohol. (Serullas, *Ann. Chim. Phys.* 46, 304.)

g. Chlorocarbonate of Ammonia.

A mixture of 1 measure of phosgene with 4 measures of ammoniacal gas condenses, with great disengagement of heat, to a white, tasteless body, which is volatile, of a saline pungent taste, and without action on vegetable colours. (J. Davy.)

Calculation.				Volume.
$2NH^3$	34·0	40·77	Ammoniacal gas	4
$COCl$	49·4	59·23	Phosgene gas	1
$2NH^3,COCl$	83·4	100·00		

When treated with aqueous phosphoric, sulphuric, or nitric acid, the compound evolves a mixture of 2 measures of hydrochloric acid with 1 measure of carbonic acid gas. Aqueous hydrochloric acid also decomposes it. Acetic acid dissolves it without effervescence. It may be sublimed in an atmosphere of carbonic acid, sulphurous acid or hydrochloric

acid gas, without undergoing decomposition. Deliquesces in the air. (John Davy.) Soluble in alcohol, but not in ether. (Regnault.)

Regnault (*Ann. Chim. Phys.* 69, 180; also *J. pr. Chem.* 18, 101) regards it as a mixture of sal-ammoniac and a compound called *Carbamide*, which contains 1 atom of carbonic oxide and 1 atom of amidogen:

$$2NH^3, COCl = NH^4Cl + NH^2, CO.$$

This view, however, has not yet been established by the actual separation of sal-ammoniac from carbamide, but is founded upon the fact that an aqueous solution of chlorocarbonate of ammonia evolves carbonic acid gas on the addition of strong nitric, hydrochloric, or sulphuric acid, but not on the addition of the same acids when dilute, or of acetic or oxalic acid; the aqueous solution, also, when supersaturated with ammonia, does not precipitate chloride of barium. Consequently, the aqueous solution does not actually contain ordinary carbonate of ammonia ready formed, but probably a compound of carbonic oxide with amidogen.

h. Chloroborate of Ammonia.

One volume of chloroboric acid gas condenses $1\frac{1}{2}$ vol. ammoniacal gas, producing a white substance which is rather less volatile than sal-ammoniac, and sublimes undecomposed. Water decomposes it, forming hydrochlorate and borate of ammonia. (Berzelius.)

i. Ammonio-terchloride of Phosphorus.

Dreifach-Chlorphosphor-Ammoniak.

Terchloride of phosphorus rapidly absorbs ammoniacal gas, the action being attended with the formation of a white cloud, and great rise of temperature. Terchloride of phosphorus freed from excess of phosphorus by repeated distillation, is surrounded with a freezing mixture and saturated with ammoniacal gas, which is very slowly evolved, so that no rise of temperature may take place. (H. Rose.) The resulting compound should be white, and dissolve slowly but completely in water; if heat is disengaged during the absorption, the substance becomes covered with brownish spots and is partially resolved into sal-ammoniac, phosphorus, and phosphide of nitrogen, the latter of which remains behind in brownish flakes on dissolving the compound in water. (H. Rose.) But even when heat is entirely avoided in its preparation, the compound gives up a large quantity of sal-ammoniac to cold water or alcohol; whence it appears to undergo partial decomposition, even at ordinary temperatures. (Wöhler & Liebig.)

White rough powder. (H. Rose.)

	Calculation.		H. Rose.		Persoz.
$5NH^3$	85·0		38·18		32·98
P	31·4		14·11		67·02
3Cl	106·2		47·71	47·31	
$5NH^3,PCl^3$	222·6		100·00		100·00

Persoz (*Ann. Chim. Phys.* 44, 321) is of opinion that the compound contains 4 atoms of ammonia to 1 atom of chloride of phosphorus.

When ammonio-terchloride of phosphorus is heated to redness in a current of carbonic acid gas, it is resolved into hydrogen, ammoniacal gas,

vapour of phosphorus, and a residue of phosphide of nitrogen. 5 atoms of the compound contain 25N, 75H, 5P, and 15Cl; in the decomposition, 15(NH^3, HCl), 2NH^3, 4PN^2 are formed, and 9H and 1P are set free; hence $\frac{4}{5}$ of the phosphorus goes to form phosphide of nitrogen. According to experiment, also, 100 parts of the compound yield 21·27 parts of phosphide of nitrogen, containing 11·18 parts of phosphorus [nearly $\frac{4}{5}$ of the phosphorus, 11·29 being the exact amount]. When the compound is heated in the open air, the same products are obtained; but the residual phosphide of nitrogen is coloured brownish-red (which changes to white every time it is heated) from the presence of phosphorus, and frequently also contains chlorine. (H. Rose.)—The quantity of hydrogen, however, which is disengaged when the compound is ignited in a current of carbonic acid gas is so small that its presence is probably accidental, arising merely from hydroscopic moisture; hence the decomposition may take place as follows:

$$2(5NH^3, PCl^3) = 6(NH^3, HCl) + 2NH^3 + N^2P + P.$$

(Wöhler & Liebig, *Ann. Pharm.* 11, 139.)—When thrown into fused potash it is violently decomposed, heat and light being disengaged, ammonia set free, and a fused mass, perfectly soluble in water, left behind. When fused with carbonate of potash or soda, it evolves ammonia and yields a residue consisting of chloride of potassium and phosphate of potash. Again, when boiled for a considerable time with an aqueous solution of pure potash or carbonate of potash, it evolves ammonia and yields a solution of chloride of potassium and phosphite of potash. (H. Rose.) Hot nitric acid dissolves it slowly but completely, with evolution of nitric oxide gas; the solution contains hydrochloric acid and phosphoric acid. Hot sulphuric acid dissolves it with disengagement of hydrochloric acid. Hydrochloric acid forms with it a solution containing phosphorous acid. (H. Rose.) The compound, when slightly moistened with concentrated hydrochloric acid, becomes strongly heated, and afterwards dissolves with ease in cold water, as though the hydrochloric acid had separated the ammonia, whereupon the chloride of phosphorus is decomposed by the water, with rise of temperature. (Wöhler & Liebig.) It dissolves slowly but completely in water; the neutral solution may be supposed to contain hydrochlorate and phosphite of ammonia,

$$5NH^3, PCl^3 + 3HO = 3(NH^3, HCl) + 2NH^3, PO^3;$$

nevertheless solution of platinum precipitates only part of the ammonia; whence the solution would appear to contain a peculiar compound of ammonia. (H. Rose.) Solution of ammonia neither decomposes nor dissolves the compound.

k. Ammonio-pentachloride of Phosphorus.

Fünffach-Chlorphosphor-Ammoniak.

It is yet doubtful whether pentachloride of phosphorus can combine with ammonia, without decomposition.

Sir H. Davy was the first who prepared this compound, viz., by *heating* chloride of phosphorus in ammoniacal gas, the gas being absorbed, with development of heat. In this manner he obtained a white inodorous, tasteless powder, which, if it had not absorbed moisture, might be heated in close vessels, even to whiteness, without alteration. [This substance was, doubtless, phosphide of nitrogen, left behind after the expulsion of

sal-ammoniac, &c.]—When exposed to the action of flame, it exhibited a slight appearance of combustion, colouring the flame yellow and leaving phosphoric acid. When fused with hydrate of potash, it burned feebly and gave off ammoniacal gas; the residue consisted of a mixture of phosphate of potash and chloride of potassium. It was not altered by boiling with water, or with sulphuric, hydrochloric, or nitric acid, or solution of potash.

Grouvelle (*Ann. Chim. Phys.* 17, 37; also *Schw.* 33, 432) obtained a compound which was immediately decomposed by solution of potash, with disengagement of ammonia, and gradually dissolved in water, yielding a solution of neutral phosphate and hydrochlorate of ammonia, so that it must have contained 1 atom of pentachloride of phosphorus to 7 atoms of ammonia.

According to H. Rose (*Pogg.* 24, 311), pentachloride of phosphorus absorbs dry ammoniacal gas with great rapidity. The resulting white mass contains 59·34 per cent. of chlorine, and consequently about 5 At. ammonia to 1 At. chloride of phosphorus. This compound, when heated out of contact of air, yields the same products of decomposition as the ammonio-terchloride of phosphorus. When thrown upon fused hydrate of potash, it forms a mixture of chloride of potassium and phosphate of potash, with disengagement of heat and light and evolution of ammonia. It is dissolved by long digestion in aqueous ammonia, carbonate of potash, nitric acid, or sulphuric acid; with the latter, however, it gives off hydrochloric acid; it also dissolves imperfectly in water.

By his more recent experiments, however, Rose has been led to doubt (*Pogg.* 52, 61) the existence of such a compound. If pentachloride of phosphorus is reduced to a very low temperature by means of a freezing mixture and ammonia slowly passed into it, the gas is scarcely if at all absorbed. When the reduction of temperature is not so great, absorption takes place, accompanied with considerable disengagement of heat; and from the mass thus saturated with ammonia, water extracts sal-ammoniac free from phosphoric acid, while phosphide of nitrogen is left undissolved.

Wöhler & Liebig also found (*Ann. Pharm.* 11, 139), that when pentachloride of phosphorus is saturated at a low temperature with ammonia, cold water merely dissolves out sal-ammoniac, unaccompanied by phosphoric acid, from the white mass obtained. But even after washing the mass for weeks, the wash-water still contained sal-ammoniac, which appeared to be obstinately retained by the phosphide of nitrogen; on boiling with potash, however, and then with dilute sulphuric or nitric acid, the sal-ammoniac was more rapidly separated. Besides sal-ammoniac and phosphide of nitrogen, Wöhler & Liebig also obtained chlorophosphide of nitrogen by the action of water (p. 474).

l. Ammonio-dichloride of Sulphur. $2NH^3,S^2Cl$.

Halb-Chlorschwefel-ammoniak. Chlorosulphite d'ammoniaque.

Vapour of dichloride of sulphur is mixed with ammoniacal gas in a glass globe. The compound may be exposed to the air for a long time without suffering decomposition. It dissolves in absolute alcohol; water precipitates sulphur from the solution, and gives rise to the formation of hydrochlorate and hyposulphite of ammonia.

$$2NH^3 + S^2Cl + HO = NH^3,HCl + NH^3,SO + S. \text{ (Martens.)}$$

m. AMMONIO-PROTOCHLORIDE OF SULPHUR.

Einfach-Chorschwefel-ammoniak.

The combination of protochloride of sulphur with ammonia is attended with great rise of temperature, whereby it may again be resolved into sal-ammoniac, nitrogen gas, and sulphur.

α. WITH 2 ATOMS OF AMMONIA.—*Chlorure de Soufre bi-ammoniacal.*

Preparation.—1. Ammoniacal gas is evolved from lime and sal-ammoniac in a flask, and first passed through a small quantity of water contained in a Woulfe's bottle, that the rapidity of its evolution may be observed—then through a long tube filled with hydrate of potash in order to dry it—and thence, through a glass tube bent at right angles—to the bottom of a glass vessel of 20 to 25 litres (4 – 6 gallons) capacity. The top of the basin is covered with two semicircular pieces of slate, &c., one of which has an opening in its centre for the passage of the ammonia tube, the other a slit so situated as to come just over the middle of the vessel. Through this slit pass four large threads united at top to a piece of wood, and connected at the other end with a flat piece of slate which is thus suspended in the basin; on the plate are put six small colour-saucers (of porous earthenware). As soon as the glass is filled with ammoniacal gas, the second piece of slate is moved a little on one side—the plate with the saucers drawn up—a few drops of protochloride of sulphur poured into each of them—and the whole again lowered into the glass; then, when the dense fumes at first produced have subsided, the plate is drawn up as before, and fresh saucers containing protochloride of sulphur are introduced. The chloride of sulphur must be perfectly saturated with chlorine, by Soubeiran's method, (p. 333). No rise of temperature must take place; hence the experiment is best performed in winter. For the same reason, it is necessary to use a large vessel, and to introduce the chloride of sulphur by small quantities at a time. The saucers also in which the chloride of sulphur is placed, must be of considerable thickness and changed every time, so that they may exert as much cooling action as possible. The glass vessel should not become sensibly warm. It is also necessary that the ammonia be in excess; otherwise, a blue and red substance is produced, which cannot, without considerable difficulty, be converted into the required compound by a subsequent excess of ammonia. When the experiment has been properly conducted, the sides and bottom of the glass vessel become covered with loose, dirty yellow flakes. The tube and plates are then removed, and a glass plate luted over the mouth of the vessel while still full of ammoniacal gas. On the following day, when the flakes have acquired a pure yellow colour, the ammoniacal gas is expelled from the vessel by a current of air, and lastly the flakes are exposed to the air in thin layers, till they no longer smell of ammonia.—2. The compound containing 1 atom of ammonia is first prepared and then exposed to an atmosphere of ammoniacal gas, till it has taken up an additional atom of ammonia. During the absorption, the compound becomes first green, and then yellow, but without any observable rise of temperature.

Pale, lemon-coloured flakes: crystallizable from a solution in ether. Inodorous.

Calculation according to Soubeiran.

$2NH^3$	34·0	39·81
SCl	51·4	60·19
$2NH^3, SCl$	85·4	100·00

In vacuo, the compound loses, in 14 hours, 0·2 per cent. of ammonia; in 48 hours, 1·6; and in 96 hours, 2·3 per cent. When gently heated in a glass tube, it first gives off pure ammoniacal gas, then the same gas mixed with nitrogen, together with sulphur and sal-ammoniac, sulphide of nitrogen being sublimed throughout the process. This decomposition commences at a temperature between 35° and 40°, continues slowly at 100°, but proceeds more rapidly between 100° and 240°, in a current of hydrogen or ammoniacal gas. Oil of vitriol decomposes the compound with violence, combining with the ammonia and setting chloride of sulphur at liberty; at the same time, however, a small quantity of chloride of sulphur escapes together with 1 atom of ammonia. Cold water likewise decomposes the compound, separating sulphide of nitrogen at first in the form of a yellow powder, and forming a yellow solution, which, in addition to hydrochlorate and hyposulphite of ammonia, contains a peculiar substance—probably a compound of NS^3, SCl with ammonia—but the yellow colour quickly disappears (more rapidly on the addition of an acid), and even the sulphide of nitrogen disappears in the course of a few days; after that, the colourless solution contains only hydrochlorate and hyposulphite of ammonia. With hot water, these changes are effected with great rapidity;

$$2NH^3,SCl + HO = NH^3,HCl + NH^3,SO.$$

The sulphide of nitrogen separated at the commencement, contains at most one-third of the sulphur present in the compound. The addition of an acid to the water does not increase this quantity. The compound prepared by the first method always leaves a small quantity of yellowish white sulphur behind when digested in water, because the heat evolved during the absorption of the ammonia by the chloride of sulphur causes a partial decomposition. This sulphur, which Gregory supposed to be sulphide of nitrogen, contains only traces of nitrogen and ammonia. The compound prepared by the second method dissolves completely in water. Alcohol, when it contains only a small quantity of water, acts on the compound like pure water.

The compound dissolves but sparingly in absolute alchohol or ether, forming a yellow solution, from which it crystallizes on evaporation, though a portion is always decomposed at the same time. (Soubeiran.)

β. With 1 Atom of Ammonia.—*Chlorure de Soufre ammoniacal.*

Preparation.—Similar to that of the compound with 2 atoms of ammonia, according to the first method, excepting that the ammoniacal gas is introduced very sparingly into the large glass, and the saucers containing the protochloride of sulphur are renewed before the red compound β is converted into the yellow compound α; but even if a small quantity of the yellow compound should be formed, it rapidly disappears on mixing it with the red, which contains a portion of free chloride of sulphur. A small quantity of ammoniacal gas is lastly introduced, in order to saturate the excess of chloride of sulphur above mentioned. (Soubeiran.)

Bulky brownish-red flakes; not volatile; have a peculiar odour resembling that of chloride of sulphur. (Soubeiran.) The compound does not redden litmus; has a saline, extremely pungent taste, and may be volatilized. (Martens.)

	Calculation.		Soubeiran.	
NH^3	17·0	24·85	24·98
S	16·0	23·39	23·39
Cl	35·4	51·76	51·63
NH^3,SCl	68·4	100·00	100·00

This compound turns yellow when heated in a tube to 110°; and if kept at that temperature for some hours, it is completely converted into a yellow mixture of sal-ammoniac, chloride of sulphur, and nitrogen, without any evolution of gas.

$$4(NH^3,SCl) = 3(NH^3,HCl) + NS^4,Cl.$$

When this mixture is more strongly heated, it yields nitrogen gas, sulphur, chloride of sulphur, and sal-ammoniac. (Soubeiran.) Oil of vitriol expels chloride of sulphur from it, and forms sulphate of ammonia. (Martens, Soubeiran.) Concentrated nitric or hydrochloric acid, however, does not expel the chloride of sulphur. (Martens.) Hot water dissolves a tolerably large quantity of the compound, and separates a soft brown substance, which, when the water is heated for a long time, first becomes paler, then assumes a greenish colour, and is finally converted into pure yellow sulphur; the solution, which is yellowish-brown at first, becomes colourless after a while, and deposits sulphur containing traces of nitrogen and ammonia, (in consequence of the decomposition of the hyposulphurous acid formed at the commencement); after this, it contains hydrochlorate and sulphite of ammonia with excess of acid. Cold water produces the same effect in the course of a few days. Solution of ammonia decomposes the liquid more rapidly, likewise separating a small and variable quantity of sulphur. (Soubeiran.) The compound does not attract moisture from the air only, unless it contains chloride of sulphur. (Soubeiran.)

It dissolves readily in alcohol and ether. The alcoholic solution is dark yellow, and on the addition of water deposits sal-ammoniac, while hyposulphurous acid remains in solution; the latter is afterwards resolved into sulphurous acid and sulphur, which carries down with it a small quantity of the original compound. Both the alcoholic and the ethereal solntion give precipitates with aqueous solutions of lead and silver salts the precipitate consisting of a mixture of metallic chloride and hyposulphite of the oxide. (Soubeiran.)

n. Carbonate of Ammonio-Chloride of Sulphur.

Carbonate of chloride of sulphur gradually absorbs a large quantity of ammoniacal gas; the compound is liquid at first, but becomes solid as the quantity of ammonia increases. Its taste is first sharp, and afterwards sulphurous. When pure, it may be sublimed without decomposition; but if even a small quantity of water is present, it fuses on exposure to heat, and gives off, first ammoniacal gas, then an ethereal liquid smelling of hydrocyanic acid, then sulphurous acid, and lastly a sublimate of hydrochlorate and sulphite of ammonia. When exposed to the air, it absorbs water of crystallization without deliquescing. Dissolves in water, probably forming a solution of carbonate, sulphite, and hydrochlorate of ammonia. (Berzelius.)

o. Sulphate of Ammonio-Chloride of Sulphur.

A quantity of pentasulphate of chloride of sulphur being cooled down to a low temperature, ammoniacal gas is very slowly passed into it, so that no rise of temperature may take place; and the tolerably saturated compound thus obtained is reduced to powder, and left in contact with ammoniacal gas for several months, the gas itself being frequently renewed. When heat is disengaged during the absorption, the compound acquires a yellow colour, from formation of anhydrous sulphite of ammon; and its aqueous solution, when treated with solution of silver, gives a precipitate which is coloured yellow from the presence of sulphide of silver.

Pure white mass.

On subliming it, a small quantity of yellow anhydrous sulphate of ammon is produced. It is not deliquescent but dissolves readily in water. The solution, when evaporated in vacuo over oil of vitriol, yields a crystalline crust which has the property of remaining moist for a long time, but, when completely dry, possesses the same composition as the original compound before solution in water.

From the aqueous solution, bichloride of platinum precipitates chloride of platinum and ammonium; chloride of barium separates only a portion of the sulphuric acid, so that the filtrate again becomes turbid after long standing; chloride of strontium gives no precipitate except on boiling; nitrate of silver throws down chloride of silver. (H. Rose.)

Calculation.			H. Rose.
$9NH^3$	153·0	32·20	
$6S$	96·0	20·20	20·350
$3Cl$	106·2	22·35	22·243
$15O$	120·0	25·25	
$4NH^3, SCl^3 + 5(NH^3, SO^3)$	475·2	100·00	

The composition of the compound is such that when it is dissolved in water, 6 atoms of anhydrous sulphate of ammon and 3 atoms of sal-ammoniac may be produced.

$$9NH^3 + SCl^3 + 5SO^3 + 3HO = 6(NH^3, SO^3) + 3(NH^3, HCl). \quad \text{(H. Rose.)}$$

p. Chloride of Iodine and Ammonium. NH^4Cl, ICl^3.

Chloroiodite d'Ammoniaque.—1. One part of iodate of ammonia is heated in a flask with 8 parts of concentrated hydrochloric acid to a temperature between 40° and 50°; and when the whole of the iodate of ammonia is dissolved, the yellow solution obtained is suffered to cool.

$$NH^3, IO^5 + 6HCl = NH^4Cl + ICl^3 + 2Cl + 5HO.$$

2. A concentrated solution of hydriodate of ammonia is saturated with chlorine gas. The salt obtained in this manner crystallizes more readily and in greater purity than the former:

$$NH^4I + 4Cl = NH^4Cl + ICl^3.$$

3. Solution of sal-ammoniac is mixed with solution of terchloride of iodine.

Long, golden-yellow crystals, which, when rapidly heated, volatilize without decomposition. When exposed to a gentle heat for a long time, the whole of the terchloride of iodine is driven off, and pure sal-ammoniac

left behind. Ammonia, potash, or soda precipitates iodine from the solution,—the two latter, with disengagement of ammonia. With other bodies this compound exhibits reactions corresponding to those of the chloride of iodine and potassium. (Filhol, *J. Pharm.* 25, 441.)

Calculation according to Filhol.

NH^4Cl	53·4	18·7
ICl^3	232·2	81·3
NH^4Cl, ICl^3	285·6	100·0

Nitrogen and Fluorine.

A. Hydrofluate of Ammonia.

a. Monohydrofluate. *Fluoride of Ammonium.*

According to Sir H. Davy, ammoniacal gas unites, without separation of water, with hydrofluoric acid evolved from a mixture of fluorspar and oil of vitriol. The anhydrous salt is also obtained by heating a dry and finely powdered mixture of 1 part of sal-ammoniac and 2¼ parts of fluoride of sodium in a platinum crucible; the cover is placed upon the crucible in an inverted position, and water frequently dropped upon it to keep it cool; the fluoride of ammonium readily sublimes on the under surface in small prisms uncontaminated with sal-ammoniac. If the mixture is *at all* moist, ammonia is disengaged at the commencement, and a corresponding quantity of bifluoride is sublimed together with the monofluoride. By the wet way, this compound can only be obtained in solution, not in the anhydrous state. (Berzelius.)

Permanent in the air; fuses when heated, and sublimes at a lower temperature than sal-ammoniac; has a very pungent, saline taste. Decomposed by potassium at a red heat into fluoride of potassium and a mixture of 2 volumes of ammoniacal gas with 1 volume of hydrogen. (H. Davy.) When exposed to the air in contact with water, it evolves ammonia, even at ordinary temperatures, and is converted into the bi-acid salt; with the aid of heat, this change is effected more rapidly. It attacks glass, not only in the state of solution, and even when the ammonia is in excess, (Wieglieb, *Crell. N. Entdeck,* 1, 13), but also, according to Berzelius, even in the dry state—being thereby converted, according to J. Davy, into ammonia and double fluoride of silicium and ammonium. A solution of the salt may be used to etch on glass. It dissolves readily in water, but sparingly in alcohol. The anhydrous salt absorbs a large quantity of ammoniacal gas, and is thereby converted into a *basic salt,* which however again loses its excess of ammonia when sublimed. (Berzelius.)

b. Bihydrofluate.—*Acid Fluoride of Ammonium.*—Prepared by evaporating an aqueous solution of the mon-acid salt at a temperature between 36° and 40°, whereby half the ammonia is expelled. (Berzelius.)—Or an aqueous solution of hydrofluosilicic acid may be decomposed by excess of ammonia; the liquid filtered from the silica through linen into a platinum dish or basin and evaporated; any remaining silica precipitated by a second addition of ammonia; and the solution again filtered, evaporated, and set aside to crystallize. (Gm.) Granular (prismatic, *Gm.*) crystals, permanent in hot air, but deliquescing at ordinary temperatures, with a creeping motion. (Berzelius, *Pogg.* 1, 17.) When heated, it volatilizes in the form of a white pungent smoke, which acts very injuriously when inhaled.

B. Ammonio-fluoride of Boron.

a. With 1 *At. Ammonia.*—A mixture of equal volumes of terfluoride of boron and ammoniacal gas condenses to a white, opaque, solid body, which, when heated in close vessels, sublimes unchanged, but, if water is present, is resolved into fluoborate of ammonia which sublimes, and boracic acid which remains behind. It dissolves in water, yielding a solution of hydrofluate and borate of ammonia—or, rather, according to Berzelius, of hydrofluate of boracic acid and ammonia, and pure borate of ammonia. (J. Davy.)

b. With 2 *At. Ammonia.*—One volume of terfluoride of boron mixed with 2 volumes of ammoniacal gas, forms a colourless and transparent liquid, which, when heated or exposed to the air, or treated with anhydrous carbonic acid or hydrochloric acid gas, gives up its excess of ammonia, and is converted into the solid compound *a.* (J. Davy.)

c. With 3 *At. Ammonia.*—One volume of terfluoride of boron combines with 3 volumes of ammoniacal gas, forming a liquid which corresponds in its properties with the compound *b.* (J. Davy.)

	Calculation.		J. Davy.		Calculation.		J. Davy.		Calculation.		J. Davy.
NH^3	17·0	20·26	20	$2NH^3$	34·0	33·7	33	$3NH^3$	51·0	43·26	43
BF^3	66·9	79·74	80	BF^3	66·9	66·3	67	BF^3	66·9	56·74	57
a.	83·9	100·00	100	*b.*	100·9	100·0	100	*c.*	117·9	103·00	100

C. Fluoborate of Ammonia.

Boracic acid expels 3 atoms of ammonia from 4 atoms of monohydrofluate of ammonia, and produces a compound of 1 atom of terhydrofluate of boracic acid with 1 atom of monohydrofluate of ammonia, that is to say, a double hydrofluate of boracic acid and ammonia;

$$4(NH^3, HF) + BO^3 = (NH^3, HF + BO^3, 3HF) + 3NH^3:$$

this again is converted by evaporation into a compound of fluoride of boron with hydrofluate of ammonia or fluoride of ammonium.

$$NH^3, HF + BO^3, 3HF = (NH^4F + BF^3) + 3HO.$$

By sublimation, it may be freed from the excess of boracic acid added at the beginning of the process. The sublimate is white, and, when deposited on the hotter parts of the vessel, fused and transparent, but never crystalline. Fluoborate of ammonia crystallizes from an aqueous solution in small six-sided prisms with dihedral summits. It tastes like sal-ammoniac, and reddens litmus. It is not changed by mixing with ammonia and subsequent evaporation. It dissolves with great facility in water, and rather freely in alcohol; the aqueous solution does not attack glass. (Berzelius.)

According to Kuhlmann, terfluoride of boron is capable of uniting with nitric oxide, nitrous, hyponitric, and nitric acids.

Nitrogen with Nitrogen.

A. Nitrite of Ammonia.

1. Prepared by decomposing nitrite of lead with sulphate of ammonia, or nitrite of silver with sal-ammoniac, and leaving the filtrate to evaporate in the air or in vacuo, at ordinary temperatures.—Or by passing

nitrous acid vapour into solution of ammonia, and evaporating over lime. (Millon.)—Imperfectly crystallized saline mass, which, when heated, is resolved into water, nitrous oxide, and ammonia. At 50°, (102° F.) the aqueous solution is decomposed, with evolution of nitrogen gas, after which it remains neutral. (*vid.* p. 372.) *Sch.* 71, (Berzelius, *Gilb.* 40, 206.)

$$NH^4O,NO^3 = 4HO + 2N.$$

¶ The decomposition is sudden or gradual, accordingly as the solution is acid or alkaline. A single drop of ammonia added to the neutral solution is sufficient to render the decomposition gradual; and a single drop of hydrochloric, nitric, or sulphuric acid, causes it to take place suddenly. On this is founded Millon's method of preparing the salt given above. (Millon, *N. Ann. Chim. Phys.* 19, 255.) ¶—With oil of vitriol, the salt behaves as with nitrate of ammonia. (Pelouze.)

	Calculation.		Berzelius.
NH^3	17	26·56	
NO^3	38	59·38	
HO	9	14·36	13·68
NH^3, HO, NO^3	64	100·00	

B. Nitrate of Ammonia.

Flammender Saltpeter, Nitrum flammans.—A neutral mixture of aqueous nitric acid and caustic ammonia or carbonate of ammonia is evaporated and set aside to crystallize.—Crystallizes in six-sided prisms with six-sided pyramids, or in thin needles; when evaporated to a very small bulk, it solidifies in a fibrous or dense amorphous mass. Sp. gr = 1·707 (Kopp.) Has a sharp, bitter, unpleasant taste.

Crystallized.					H. Davy.			Ure.
	Calculation.		Berzelius.	Kirwan.	Prismatic.	Fibrous.	Amorphous.	
NH^3	17·0	21·25	21·143	23	18·4	19·3	19·8	23·3
NO^5	54·0	67·50	67·625	57	69·5	72·5	74·5	65·0
HO	9·0	11·25	11·232	20	12·1	8·2	5·7	11·7
NH^3,HO,NO^5	80·0	100·00	100·000	100	100·0	100·0	100·0	100·0

According to Dumas, the crystals contain not 1, but 2 atoms of water.

When exposed to the air, it loses ammonia and acquires an acid reaction. (Emmet.) When exposed to a gradually increasing heat, it *fuses* and is resolved, with effervescence, into nitrous oxide gas and aqueous vapour. (*Sch.* 72.)

$$NH^3 + NO^5 = 2NO + 3HO.$$

The salt fuses imperfectly at 56° (133° F.), perfectly at 108° (226° F.); at 150° (302° F.) it evolves white fumes which condense in drops; at 175° (347° F.) it effervesces slightly; at 225° (437° F.) rapidly; at 238° (460° F.) it begins to evolve nitrous oxide; and at 250° (482° F.) this gas is evolved in abundance. At this temperature, which remains constant for a long time, a small quantity of nitrate of ammonia sublimes unchanged. The residual salt (if any is left undecomposed) solidifies in a crystalline form on cooling. (Pleischl.) At 180° (356° F.) the salt boils without being decomposed, as decomposition does not begin below a temperature of between 190° and 200°. (Legrand, *Ann. Chim. Phys.* 59, 435.) Under increased pressure the decomposition requires a higher temperature. (Niemann.) (p. 374.)—If nitrate of ammonia is mixed with

an equal weight of chloride of calcium, the mixture when heated evolves, not nitrous oxide, but nitrous acid, chlorine, and nitrogen gas, after which sal-ammoniac sublimes, and a mixture of lime and chloride of calcium is left behind. A mixture of equal weights of nitrate of ammonia and chloride of potassium, yields on exposure to heat, nitrogen gas, chlorine, sublimed sal-ammoniac, and a residue consisting of nitrate of potash and chloride of potassium. (Pleischl, *Schw.* 38, 462.)—If nitrate of ammonia is heated so strongly that the vessel becomes filled with white fumes, nitric oxide, nitrite of ammonia, and free ammonia are evolved, as well as nitrous oxide. (Berzelius.) When rapidly and violently heated, as, for instance, when thrown on a red-hot porcelain plate, it burns with a pale-yellow light, and very slight noise, and gives off water, nitrous acid and nitrogen gas.—It explodes when thrown on red-hot charcoal. Phosphorus thrown into the fused salt burns with a brilliant light and forms phosphoric acid—unless the phosphorus is in excess, in which case phosphoric oxide is the principal product. (Marchand, *J. pr. Chem.* 13, 442.)—Sulphur undergoes no change by contact with the fused salt, but most of the metals are oxidized by it. Zinc disappears as rapidly in the fused salt as in an acid, and evolves so much heat, that the further application of heat from without is rendered unnecessary, the temperature quickly rising from between 138° and 160°, at which the action on the zinc commences, to 260°. During the action, nitrogen, ammoniacal gas, and water are evolved, but no nitrous or nitric oxide. Lead is also rapidly oxidized, with disengagement of nitric oxide and hyponitrous acid. Antimony, bismuth, nickel, copper, and silver are oxidized slowly; arsenic, tin, iron, and mercury, not at all. (Emmet.) Silver disengages nitric oxide without nitrous oxide and forms ammonio-nitrate of silver. Spongy platinum likewise appears to disengage nitric oxide only, and form an insoluble platinum compound. (L. A. Buchner, *Repert.* 39, 360.)—A mixture of nitrate of ammonia and sal-ammoniac in a state of fusion dissolves gold; and if a small quantity of nitrate or chlorate of potash be added, it oxidizes and dissolves the whole of the metals, even gold, platinum, rhodium, and iridium. This mixture likewise dissolves titaniferous schorl, chrome iron ore, sulphide of molybdenum, and pitchblende, and in short, the greater number of the metallic oxides. Litharge, at ordinary temperatures, expels ammonia from the solid salt. (Emmet, *Sill. Amer. J.* 18, 255.)—Nitrate of ammonia, when treated with a small quantity of oil of vitriol, is resolved into sulphate of ammonia and free nitric acid; the same result is obtained when a solution of the salt, (dried as perfectly as possible,) in 50 times its weight of oil of vitriol, is heated merely to a temperature between 90° and 120°; but on heating it to 150°, it evolves nitrous oxide gas mixed with a small quantity of nitric oxide, hyponitric acid, and nitric acid vapour, and leaves a mixture of oil of vitriol and water. When the quantity of oil of vitriol is only 10 times that of the salt, about $\frac{3}{4}$ of the latter is resolved into sulphate of ammonia and nitric acid, and $\frac{1}{4}$ into nitrous oxide and water. (Pelouze, *Ann. Chim. Phys.* 77, 47; also *Ann. Pharm.* 39, 312.) One part of nitrate of ammonia dissolves in 0·502 parts of water at 18° (Karsten), with great reduction of temperature; it dissolves in a smaller quantity of hot water. Deliquesces in the air.

C. Sulphite of Nitric Oxide and Ammonia.

Nitrosulphate of Ammonia, Nitrosulfate d'Ammoniaque.—When an aqueous solution of sulphite of ammonia, previously cooled down by a freezing mixture till it begins to congeal, is brought in contact with nitric oxide gas, it absorbs the gas gradually and completely, and yields crystals. —At and above 0°, nitric oxide gas decomposes an aqueous solution of sulphite of ammonia, forming sulphate of ammonia and a half volume of nitrous oxide gas. But if a concentrated solution of sulphite of ammonia is mixed with 5 times its bulk of aqueous ammonia, the absorption of nitric oxide gas and deposition of crystals take place even at temperatures above 0°, without formation of nitrous oxide. Hence an excess of ammonia prevents the decomposition of the double sulphite of nitric oxide and ammonia.—The crystals obtained are washed with aqueous ammonia —which prevents their decomposition, and also dissolves them less freely than pure water—and finally dried between folds of bibulous paper.

Colourless, transparent, rhombic prisms; neutral towards vegetable colours; of pungent and slightly bitter taste.

Calculation, according to Pelouze.

NH^3	17	19·32
NO^2	30	34·33
SO^2	32	36·36
HO	9	10·23
$NH^3, NO^2, SO^2, + HO$	88	100·00

In the dry state, the salt remains unchanged at 110°; at a somewhat higher temperature it is decomposed, with explosion and disengagement of nitrous oxide gas. When thrown on glowing coals, it is decomposed with emission of sparks. It gradually deliquesces in the air, evolving nitrous oxide gas and yielding pure sulphate of ammonia. In water it dissolves at first without decomposition, but is afterwards resolved—the more rapidly, the higher the temperature—into nitrous oxide gas and solution of sulphate of ammonia:

$$NH^3, NO^2, SO^2 = NH^3, SO^3 + NO.$$

At 0°, the decomposition is effected very slowly; at 40°, with rapid effervescence.—A solution of the compound in aqueous ammonia is decomposed in the same manner, but much more slowly. The decomposition of the aqueous solution is very much hastened by the addition of charcoal, peroxide of manganese, oxide of silver, metallic silver, and spongy platinum, which nevertheless do not thereby undergo any chemical change (I., 114, 115). Excess of ammonia prevents this rapid decomposition. The stronger acids, also, even aqueous solution of carbonic acid, and solutions of sesqui-chloride of chromium, sulphate of ferrous oxide, sulphate of copper, sulphate of ferric oxide, corrosive sublimate, nitrate of silver and acetate of lead give rise—even at some degrees below 0°—to rapid decomposition, accompanied with rapid evolution of nitrous oxide gas, whilst sulphuric acid and ammonia remain in the liquid.—The salt does not dissolve in alcohol, even when hot, and is precipitated from an aqueous solution on the addition of that liquid. (Pelouze, *Ann. Chim. Phys.* 60, 151.)

D. Compound of Ammonio-chloride of Sulphur with Ammonio-sulphide of Nitrogen.

$NH^3, NS + NH^3SCl$.

Formation. When protochloride of sulphur is slowly dropped into an aqueous solution of ammonia, a dark, brownish-red, soft substance is precipitated, with great rise of temperature and formation of dense fumes, but no evolution of gas; the same substance is likewise produced, but without the fumes, when the chloride of sulphur is poured through a funnel to the bottom of a vessel filled with solution of ammonia.—The supernatant liquid contains hydrochlorate, hyposulphite, and sulphate of ammonia, besides a small quantity of sulphur mechanically suspended. If a larger quantity of chloride of sulphur is used, the saturated liquid assumes a lilac tint; after which, heat is evolved and the mixture becomes milky from separation of sulphur. If the brownish-red substance is left in the liquid, it continually becomes paler and is converted into Gregory's light-yellow sulphide of nitrogen (p. 443). If, on the contrary, it is removed from the liquid immediately after its formation, it rapidly becomes heated, swells up, and is soon converted into the same pale yellow substance. Again, if it is freed as soon as possible from the supernatant liquid by trituration with cold water, collected on a filter, and pressed between folds of bibulous paper, a powder is obtained which likewise rapidly becomes heated, swells up, and changes into the pale-yellow compound.

Preparation.—Protochloride of sulphur is added, with constant stirring, to aqueous ammonia diluted with an equal bulk of water, the quantities being so regulated that the liquid may remain alkaline, and not be very strongly heated.

The red substance formed is immediately thrown on a linen filter, pressed flat in cold water, in order to keep it cool, and worked up with fresh quantities of water.

Brownish red.

Decompositions.—1. This substance, when kept under water, is decomposed in the course of a couple of days, without disengagement of gas; but a small quantity of a yellow substance is separated, and a solution formed, containing hydrochlorate and hyposulphite of ammonia with a small quantity of free ammonia. If the hyposulphurous acid be converted into sulphuric acid by heating the liquid with chloride of soda, it is found that 4 atoms of sulphuric acid are present for each atom of hydrochloric acid. According to the formula given by Soubeiran, the red compound should yield a neutral solution.

$$NH^3, NS^3 + NH^3, SCl + 4HO = NH^3, HCl + 2(NH^3, S^2O^2).$$

No yellow powder is formed when the ammonia used in the preparation of the original red compound is cold and concentrated; but a large quantity separates if the ammonia has been previously warmed and weakened by the addition of chloride of sulphur, because in that case, sulphur is precipitated.—2. The red compound imparts a red colour to solution of ammonia. (Soubeiran.)

OTHER COMPOUNDS OF NITROGEN.

a. With metals; *Metallic Nitrides, Azotures Metalliques, Stickstoff-metalle.*—1. A few metallic oxides and chlorides, when heated to a certain temperature in ammoniacal gas, are converted into metallic nitrides having the form of brown or green powders, which are decomposed at higher temperatures, sometimes with explosion; such is the case with sesquichloride of chromium, protoxide of copper, protoxide of mercury, &c., *e.g.*

$$3HgO + NH^3 = Hg^3N + 3HO.$$

2. Ammoniacal gas is much more easily resolved into its elements when passed through a tube containing red-hot iron or copper, than when passed through an empty tube at the same temperature (p. 421). The metals are thereby rendered brittle; their specific gravity is diminished; and in some cases their colour is altered; frequently also they sustain an increase of weight, due to the nitrogen which they have taken up. On the other hand, the physical characters of the metal are often altered without increase of weight—possibly because the nitride formed at the beginning of the action loses its nitrogen at a later period (vid. *Potassium, Chromium, Iron, Copper, Mercury*).

b. Nitrogen is a frequent constituent of organic compounds.

APPENDIX.

TABLE I.

For converting French Decimal Measures and Weights into English Measures and Weights.

A. Measures of Length.

	1	2	3	4	5	6	7	8	9
Metre.									
Engl. Yards	1·09363	2·18727	3·28090	4·37453	5·46816	6·56180	7·65543	8·74906	9·84270
„ Feet	3·28090	6·56180	9·84270	13·12360	16·40450	19·68539	22·96629	26·24719	29·52809
„ Inches	39·37080	78·74158	118·11236	157·48315	196·85394	236·22473	275·59552	314·96630	354·33709
Decimetre.									
Feet	0·32809	0·65618	0·98427	1·31236	1·64045	1·96854	2·29663	2·62472	2·95281
Inches	3·93708	7·87416	11·81124	15·74832	19·68539	23·62247	27·55955	31·49663	35·43371
Centimetre.									
Inches	0·39371	0·78742	1·18112	1·57483	1·96854	2·36225	2·75596	3·14966	3·54337
Millimetre.									
Inches	0·03937	0·07874	0·11811	0·15748	0·19685	0·23623	0·27560	0·31497	0·35434

B. Measures of Capacity.

	1	2	3	4	5	6	7	8	9
Cubic Centimetre.									
Cubic Inch	0·06103	0·12205	0·18308	0·24411	0·30514	0·36616	0·42719	0·48822	0·54924
Litre.									
Engl. Imp. Gallons	0·22017	0·44033	0·66050	0·88066	1·10083	1·32100	1·54116	1·76133	1·98149
„ „ Quarts	0·88066	1·76133	2·64199	3·52266	4·40332	5·28398	6·16465	7·04531	7·92598
„ „ Pints	1·76133	2·52266	5·28399	7·04531	8·80664	10·56797	12·32930	14·09062	15·85195
Stere.									
Gallons	220·16643	440·33287	660·49930	880·66574	1100·83217	1320·99860	1541·16504	1761·33147	1981·49791

C. Weights.

	1	2	3	4	5	6	7	8	9
Kilogramme.									
Cwt.	0·01970	0·03939	0·05909	0·07879	0·09848	0·11818	0·13788	0·15758	0·17727
lb. (avoird.)	2·20486	4·40971	6·61457	8·81943	11·02428	13·22914	15·43400	17·63886	19·84371
Kilogramme.									
lb. (troy)	2·67951	5·35903	8·03854	10·71805	13·39757	16·07708	18·75659	21·43610	24·11562
Gramme.									
Grains	15·44242	30·88484	46·32726	61·76968	77·21210	92·65352	108·09694	123·53936	138·98178
Decigramme.									
Grains	1·54424	3·08848	4·63273	6·17697	7·72121	9·26535	10·80969	12·35394	13·89818
Centigramme.									
Grains	0·15442	0·30885	0·46327	0·61770	0·77212	0·92654	1·08097	1·23530	1·38982
Milligramme.									
Grains	0·01544	0·03089	0·04633	0·06177	0·07721	0·09265	0·10810	0·12354	0·13898

These tables are arranged on the same plan as the Analytical Tables in Rose's "*Analytical Chemistry,*" and other works of similar character. One example may suffice to illustrate the mode of using them. Let it be required to find how many grains are equal to 87·435 grammes:—

By Column 8 line 4 of Table C, we find:	80	grammes	=	1235·3936	grains.
„ 7 „ 4 „ „ „	7	„	=	108·0969	„
„ 4 „ 5 „ „ „	·4	„	=	6·1770	„
„ 3 „ 6 „ „ „	·03	„	=	0·4633	„
„ 5 „ 7 „ „ „	·005	„	=	0·0772	„
	87·435	grammes	=	1350·2080	grains.

TABLE II.

Barometer Scale in Millimetres and Inches.

Mm.		In.	Mm.		In.	Mm.		In.
700	=	27·560	730	=	28·741	760	=	29·922
701	=	27·590	731	=	28·780	761	=	29·961
702	=	27·638	732	=	28·819	762	=	30·000
703	=	27·678	733	=	28·859	763	=	30·040
704	=	27·717	734	=	28·898	764	=	30·079
705	=	27·756	735	=	28·938	765	=	30·119
706	=	27·795	736	=	28·977	766	=	30·158
707	=	27·835	737	=	29·016	767	=	30·197
708	=	27·876	738	=	29·056	768	=	30·237
709	=	27·914	739	=	29·095	769	=	30·276
710	=	27·953	740	=	29·134	770	=	30·316
711	=	27·992	741	=	29·174	771	=	30·355
712	=	28·032	742	=	29·213	772	=	30·384
713	=	28·071	743	=	29·252	773	=	30·434
714	=	28·111	744	=	29·292	774	=	30·473
715	=	28·150	745	=	29·331	775	=	30·512
716	=	28·189	746	=	29·371	776	=	30·552
717	=	28·229	747	=	29·410	777	=	30·591
718	=	28·268	748	=	29·449	778	=	30·631
719	=	28·308	749	=	29·489	779	=	30·670
720	=	28·347	750	=	29·528	780	=	30·709
721	=	28·386	751	=	29·567	781	=	30·749
722	=	28·426	752	=	29·607	782	=	30·788
723	=	28·465	753	=	29·646	783	=	30·827
724	=	28·504	754	=	29·685	784	=	30·867
725	=	28·543	755	=	29·725	785	=	30·906
726	=	28·583	756	=	29·764	786	=	30·945
727	=	28·622	757	=	29·804	787	=	30·985
728	=	28·661	758	=	29·843	788	=	31·024
729	=	28·701	759	=	29·882	789	=	31·063

28 inches	=	711·187	millimetres.
29 „	=	736·587	„
30 „	=	761·986	„
31 „	=	787·386	„

1 millimetre	=	0·03937	inch.
·1 „	=	0·00394	„
·01 „	=	0·00039	„

·1 inch	=	25·39954	millimetres.
·1 „	=	2·53995	„
·01 „	=	0·25400	„
·001 „	=	0·02540	„

TABLE III.

For converting degrees of the Centigrade thermometer into degrees of Fahrenheit's Scale.

Cent.	Fah.	Cent.	Fah.	Cent.	Fah.
− 100°	− 148·0°	− 50°	− 58·0°	0°	+ 32·0°
99	146·2	49	56·2	+ 1	33·8
98	144·4	48	54·4	2	35·6
97	142·6	47	52·6	3	37·4
96	140·8	46	50·8	4	39·2
95	139·0	45	49·0	5	41·0
94	137·2	44	47·2	6	42·8
93	135·4	43	45·4	7	44·6
92	133·6	42	43·6	8	46·4
91	131·8	41	41·8	9	48·2
90	130·0	40	40·0	10	50·0
89	128·2	39	38·2	11	51·8
88	126·4	38	36·4	12	53·6
87	124·6	37	34·6	13	55·4
86	122·8	36	32·8	14	57·2
85	121·0	35	31·0	15	59·0
84	119·2	34	29·2	16	60·8
83	117·4	33	27·4	17	62·6
82	115·6	32	25·6	18	64·4
81	113·8	31	23·8	19	66·2
80	112·0	30	22·0	20	68·0
79	110·2	29	20·2	21	69·8
78	108·4	28	18·4	22	71·6
77	106·6	27	16·6	23	73·4
76	104·8	26	14·8	24	75·2
75	103·0	25	13·0	25	77·0
74	101·2	24	11·2	26	78·8
73	99·4	23	9·4	27	80·6
72	97·6	22	7·6	28	82·4
71	95·8	21	5·8	29	84·2
70	94·0	20	4·0	30	86·0
69	92·2	19	2·2	31	87·8
68	90·4	18	0·4	32	89·6
67	88·6	17	+ 1·4	33	91·4
66	86·8	16	3·2	34	93·2
65	85·0	15	5·0	35	95·0
64	83·2	14	6·8	36	96·8
63	81·4	13	8·6	37	98·6
62	79·6	12	10·4	38	100·4
61	77·8	11	12·2	39	102·2
60	76·0	10	14·0	40	104·0
59	74·2	9	15·8	41	105·8
58	72·4	8	17·6	42	107·6
57	70·6	7	19·4	43	109·4
56	68·8	6	21·2	44	111·2
55	67·0	5	23·0	45	113·0
54	65·2	4	24·8	46	114·8
53	63·4	3	26·6	47	116·6
52	61·6	2	28·4	48	118·4
51	59·8	1	30·2	49	120·2

TABLE III.—(*continued.*)

Cent.	Fah.	Cent.	Fah.	Cent.	Fah.
+ 50°	+ 122·0°	+ 100°	+ 212·0°	+ 150°	+ 302·0°
51	123·8	101	213·8	151	303·8
52	125·6	102	215·6	152	305·6
53	127·4	103	217·4	153	307·4
54	129·2	104	219·2	154	309·2
55	131·0	105	221·0	155	311·0
56	132·8	106	222·8	156	312·8
57	134·6	107	224·6	157	314·6
58	136·4	108	226·4	158	316·4
59	138·2	109	228·2	159	318·2
60	140·0	110	230·0	160	320·0
61	141·8	111	231·8	161	321·8
62	143·6	112	233·6	162	323·6
63	145·4	113	235·4	163	325·4
64	147·2	114	237·2	164	327·2
65	149·0	115	239·0	165	329·0
66	150·8	116	240·8	166	330·8
67	152·6	117	242·6	167	332·6
68	154·4	118	244·4	168	334·4
69	156·2	119	246·2	169	336·2
70	158·0	120	248·0	170	338·0
71	159·8	121	249·8	171	339·8
72	161·6	122	251·6	172	341·6
73	163·4	123	253·4	173	343·4
74	165·2	124	255·2	174	345·2
75	167·0	125	257·0	175	347·0
76	168·8	126	258·8	176	348·8
77	170·6	127	260·6	177	350·6
78	172·4	128	262·4	178	352·4
79	174·2	129	264·2	179	354·2
80	176·0	130	266·0	180	356·0
81	177·8	131	267·8	181	357·8
82	179·6	132	269·6	182	359·6
83	181·4	133	271·4	183	361·4
84	183·2	134	273·2	184	363·2
85	185·0	135	275·0	185	365·0
86	186·8	136	276·8	186	366·8
87	188·6	137	278·6	187	368·6
88	190·4	138	280·4	188	370·4
89	192·2	139	282·2	189	372·2
90	194·0	140	284·0	190	374·0
91	195·8	141	285·8	191	375·8
92	197·6	142	287·6	192	377·6
93	199·4	143	289·4	193	379·4
94	201·2	144	291·2	194	381·2
95	203·0	145	293·0	195	383·0
96	204·8	146	294·8	196	384·8
97	206·6	147	296·6	197	386·6
98	208·4	148	298·4	198	388·4
99	210·2	149	300·2	199	390·2

TABLE III.—(*continued.*)

Cent.	Fah.	Cent.	Fah.	Cent.	Fah.
+ 200°	+ 392·0°	+ 250°	+ 482·0°	+ 300°	+ 572·0°
201	393·8	251	483·8	301	573·8
202	395·6	252	485·6	302	575·6
203	397·4	253	487·4	303	577·4
204	399·2	254	489·2	304	579·2
205	401·0	255	491·0	305	581·0
206	402·8	256	492·8	306	582·8
207	404·6	257	494·6	307	584·6
208	406·4	258	496·4	308	586·4
209	408·2	259	498·2	309	588·2
210	410·0	260	500·0	310	590·0
211	411·8	261	501 8	311	591·8
212	413·6	262	503·6	312	593·6
213	415·4	263	505·4	313	595·4
214	417·2	264	507·2	314	597·2
215	419·0	265	509·0	315	599·0
216	420·8	266	510·8	316	600·8
217	422·6	267	512·6	317	602·6
218	424·4	268	514·4	318	604·4
219	426·2	269	516·2	319	606·2
220	428·0	270	518·0	320	608·0
221	429·8	271	519·8	321	609·8
222	431·6	272	521·6	322	611·6
223	433·4	273	523·4	323	613·4
224	435·2	274	525·2	324	615·2
225	437·0	275	527·0	325	617·6
226	438·8	276	528·8	326	618·8
227	440·6	277	530·6	327	620·6
228	442·4	278	532·4	328	622·4
229	444·2	279	534·2	329	624·2
230	446·0	280	536·0	330	626·0
231	447·8	281	537·8	331	627·8
232	449·6	282	539·6	332	629·6
233	451·4	283	541·4	333	631·4
234	453·2	284	543·2	334	633·2
235	455·0	285	545.0	335	635·0
236	456·8	286	546·8	336	636·8
237	458·6	287	548·6	337	638·6
238	460·4	288	550·4	338	640·4
239	462·2	289	552·2	339	642·2
240	464·0	290	554·0	340	644·0
241	465·8	291	555·8	341	645·8
242	467·6	292	557·6	342	647·6
243	469·4	293	559·4	343	649·4
244	471·2	294	561·2	344	651·2
245	473·0	295	563·0	345	653·0
246	474·8	296	564·8	346	654·8
247	476·6	297	566·6	347	656·6
248	478·4	298	568·4	348	658·4
249	480·2	299	570·2	349	660·2

TABLE IV.

Showing the elastic force of condensable gases in the state of maximum tension. (Faraday, *Phil. Trans.* 1845.)

The marked temperatures are those which were determined by actual experiment.

Carbonic Acid.

Temp. Fah.	Tension in Atmosphere.	Temp. Fah.	Tension in Atmosphere.	Temp. Fah.	Tension in Atmosphere.
—*111°	1·14	— 60°	6·97	—* 4	21·48
110	1·17	*56	7·70	0	22·84
*107	1·36	50	8·88	+* 5	24·75
100	1·85	40	11·07	*10	26·82
* 95	2·28	*34	12·50	*15	29·09
90	2·77	30	13·54	20	30·65
* 83	3·60	*23	15·45	*23	33·15
80	3·93	20	16·30	30	37·00
* 75	4·60	*15	17·80	*32	38·50
70	5·33	10	19·38		

Sulphurous Acid.

Temp. Fah.	Tension in Atmosphere.	Temp. Fah.	Tension in Atmosphere.	Temp. Fah.	Tension in Atmosphere.
0°	0·725	+ 40°	1·78	+ 76·8°	3·50
+ 10	0·920	46·5	2·00	85	4·00
*14	1·00	*48	2·06	*90	4·35
*19	1·12	*56	2·42	93	4·50
*23	1·23	58	2·50	98	5·00
*26	1·33	*64	2·76	*100	5·16
31·5	1·50	68	3·00	104	5·50
*32	1·53	*73·5	3·28	110	6·00
*33	1·57				

Hydrosulphuric Acid.

Temp. Fah.	Tension in Atmosphere.	Temp. Fah.	Tension in Atmosphere.	Temp. Fah.	Tension in Atmosphere.
— 100°	1·02	— 50°	2·35	0°	6·10
*94	1·09	45	2·59	+ *10	7·21
90	1·15	40	2·86	20	8·44
*83	1·27	30	3·49	*26	9·36
80	1·33	*24	3·95	30	9·94
*74	1·50	*20	4·24	40	11·84
70	1·59	*16	4·60	*48	13·70
*68	1·67	10	5·11	50	14·14
60	1·93	* 2	5·90	*52	14·60
*58	2·00				

TABLE IV.—(*continued.*)

Hydrochloric Acid.

Temp. Fah.		Tension in Atmosphere.	Temp. Fah.		Tension in Atmosphere.	Temp. Fah.		Tension in Atmosphere.
— 100°	...	1·80	—*53°	...	5·83	—* 5°	...	13·88
* 92	...	2·28	50	...	6·30	* 0	...	15·04
90	...	2·38	*42	...	7·40	+ 10	...	17·74
* 83	...	2·90	40	...	7·68	20	...	21·09
80	...	3·12	*33	...	8·53	*25	...	23·08
* 77	...	3·37	30	...	9·22	30	...	25·32
70	...	4·02	*22	...	10·66	*32	...	26·20
* 67	...	4·26	20	...	10·92	40	...	30·67
60	...	5·08	10	...	12·82			

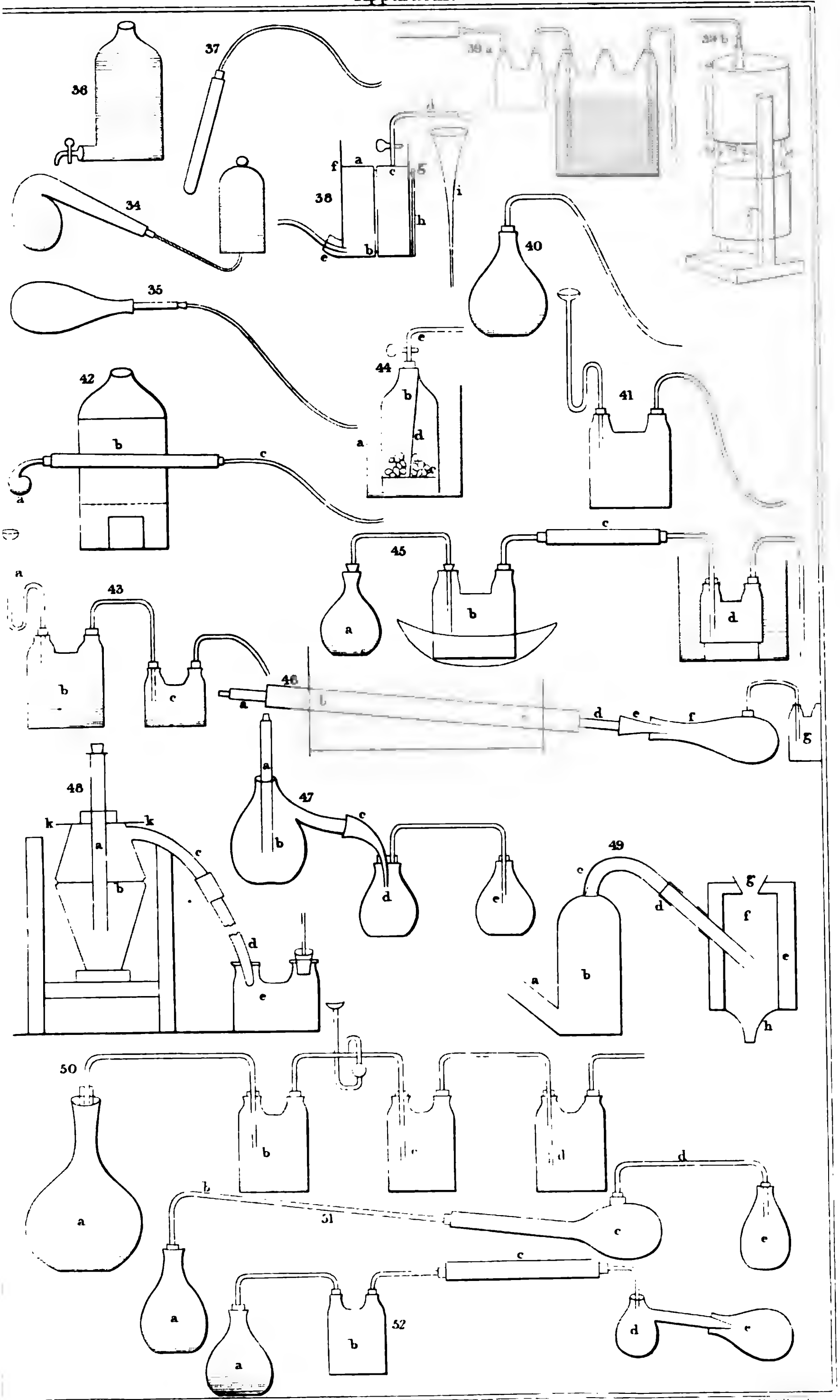
Nitrous Oxide.

Temp. Fah.		Tension in Atmosphere.	Temp. Fah.		Tension in Atmosphere.	Temp. Fah.		Tension in Atmosphere.
— 125°	...	1·00	— 70°	...	4·11	—15°	...	14·69
120	...	1·10	65	...	4·70	10	...	16·15
115	...	1·22	60	...	5·36	5	...	17·70
110	...	1·37	55	...	6·09	0	...	19·34
105	...	1·55	50	...	6·89	+ 5	...	21·07
100	...	1·77	45	...	7·76	10	...	22·89
95	...	2·03	40	...	8·71	15	...	24·80
90	...	2·34	35	...	9·74	20	...	26·80
85	...	2·70	30	...	10·85	25	...	28·90
80	...	3·11	25	...	12·04	30	...	31·10
75	...	3·58	20	...	13·32	35	...	33·40

*The temperatures in this table are all within half a degree of those actually observed.

Ammonia.

Temp. Fah.		Tension in Atmosphere.	Temp. Fah.		Tension in Atmosphere.	Temp. Fah.		Tension in Atmosphere.
*0°	...	2·48	+*41°	...	5·10	+*61·3°	...	7·00
+ 0·5	...	2·50	*44	...	5·36	*65·6	...	7·50
*9·3	...	3·00	*45	...	5·45	*67	...	7·63
*18	...	3·50	45·8	...	5·50	69·4	...	8·00
*21	...	3·72	*49	...	5·83	73	...	8·50
25·8	...	4·00	*51·4	...	6·00	76·8	...	9·00
*26	...	4·04	*52	...	6·10	80	...	9·50
*32	...	4·44	*55	...	6·38	*83	...	10·00
*33	...	4·50	*56·5	...	6·50	85	...	10·30
39·5	...	5·00	*60	...	6·90			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